

AD620513

#5023:1

RIAS

TECHNICAL REPORT

65-7

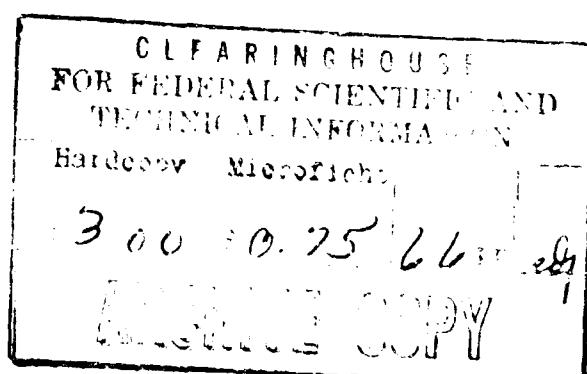
AUGUST 1965

ON THE MECHANISM(S) OF
STRESS-CORROSION CRACKING

By

E.N. PUGH

F D D C
F SEP 16 1965
TIGW B



MARTIN

ON THE MECHANISM(S) OF STRESS-CORROSION CRACKING

by

E. N. Pugh

First Technical Report to A.R.O.(D)

Army Research Office (Durham) Project

DA-31-124-ARO-D-258

August 1965

Reproduction in whole or in part is permitted for any
purpose of the United States Government

Research Institute for Advanced Studies
(Martin Co.)
1450 S. Rolling Road
Baltimore, Maryland 21227

ABSTRACT

A critical review has been made of some of the major theories of stress-corrosion cracking, with particular reference to the long-standing question of whether a single, generalized mechanism exists. It is concluded, largely on the basis of recent studies of α -brass and of aged aluminum alloys, that several different mechanisms are in fact operative in different systems, so that stress-corrosion cracking must be regarded as a generic term. Consideration is given to areas which require further study.

To be published in Proc. Conf. on "Environment-Sensitive Mechanical Behavior," Baltimore, Maryland, June 1965.

INTRODUCTION

Stress-corrosion cracking is probably the most widely studied yet least understood aspect of environment-sensitive mechanical behavior. The confusion existing in this area is reflected by the fact that the term itself lacks a precise or universally accepted definition. In general terms, it can be described as an embrittlement* process which occurs in metals, or to be more specific, in metallic alloys, when they are stressed in certain corrosive environments. There is some difference of opinion concerning the nature of the corrosive environments. Some workers^{1,2} consider that the term stress-corrosion cracking includes failures induced by (i) aqueous environments, (ii) liquid metals, and (iii) hydrogen. However, it is more common to confine the term to case (i), referring to cases (ii) and (iii) as liquid-metal embrittlement and hydrogen embrittlement, respectively. This convention is adopted in the present paper.

There have been several attempts to formulate a more precise definition of stress-corrosion cracking. For example, it has been claimed³ that "the term stress corrosion (cracking) implies a greater deterioration in the mechanical properties of the material through the simultaneous action of static stress and exposure to corrosive environment than would occur by the separate but additive action of those agencies". It will be seen below

* The term embrittlement is used to denote a reduction in macroscopic ductility; it does not imply that the fracture process is necessarily brittle, or that the mechanical properties of the material become permanently impaired by exposure to stress-corrosion conditions.

that the two main conditions of this statement, (i) that stress and corrosion must act simultaneously, and (ii) that stress must be static, are not necessary in all cases.

It is usual to accept that the term stress-corrosion cracking applies only to metals. This probably results from an early theory⁴ which considered that stress-corrosion cracking is basically an electrochemical phenomenon. However, Westwood et al.⁵⁻⁸ have demonstrated that brittle, intercrystalline cracking occurs in the non-metal silver chloride when it is stressed in aqueous environments containing certain silver complex ions, and that the failure exhibits many phenomenological similarities with stress-corrosion cracking in metals. At the present time, the question of whether the failure in silver chloride should be termed stress-corrosion cracking is purely one of semantics.

These questions of terminology stem directly from the fact that the mechanism of stress-corrosion cracking is not understood. Moreover, it is not known with certainty whether a single generalized mechanism exists or whether stress-corrosion cracking is simply a generic term. The purpose of this paper is to critically examine the major mechanisms which have been proposed to explain stress-corrosion cracking. Inevitably, a recurring theme in such a paper is the question of whether a generalized mechanism exists.

Before discussing the proposed mechanisms, it is necessary to consider the characteristics of the failures.

CHARACTERISTICS OF STRESS-CORROSION CRACKING

Stress-corrosion cracking has been observed in a wide variety of commercially important materials. For example, it occurs in aluminum alloys, brasses, steels - both mild and stainless, magnesium alloys, and titanium alloys. The characteristics of the failures are well documented⁹⁻¹⁴, so that in most cases they need only be briefly outlined.

The main characteristics which must be taken into account are:

- (1). Cracking is intercrystalline in some cases (e.g. aluminum alloys, mild steel) and transcrystalline in others (e.g. austenitic stainless steels). In some materials, magnesium-base alloys for example, either type of failure can be produced by controlling the heat treatment¹⁵. Cracking in α -brass can be either trans- or intercrystalline depending on the pH of the environment¹⁶.
- (2). The environments which cause stress-corrosion cracking appear to be specific. Thus a number of aqueous solutions may produce general or even preferential attack in a particular material, but only certain of these will cause stress-corrosion cracking. For example, mild steels crack in nitrates and alkalis but not in chlorides, sulphates or perchlorates¹⁷. On the other hand, failures in austenitic stainless steels appear to be confined to environments containing halides, principally chlorides, and caustic alkalis^{18,19}. The classical example occurs in α -brass, which traditionally has been considered to stress-corrode only in the combined presence

of ammonia (or certain ammonia derivatives), water and air²⁰. However, recent work indicates that stress-corrosion cracking in α -brass also can occur in solutions containing either nitric acid or cupric nitrate^{21,22}.

(3). Stresses which cause stress-corrosion cracking may be residual or externally applied but they must be tensile. The magnitude of the stresses can be considerably below those required to cause fracture in the absence of the environment. Fig. 1 illustrates the relationship between engineering stress and stress-corrosion lifetime for a polycrystalline magnesium-base alloy statically loaded in an aqueous sodium chloride - sodium chromate solution²³. It can be seen that the time to failure, t_F , increases with decreasing stress, and that a limiting stress level exists, σ_c , below which cracking does not occur in finite times. This limiting value is somewhat higher than the flow stress, σ_f , for this material, determined in dynamic tests. This relationship between t_F and the magnitude of the static stress is characteristic of many stress-corrosion systems²⁴. In many cases, the limiting stress level has been observed to approximate the flow stress^{25,26}. However, failures in α -brass have been observed under certain conditions at significantly lower stresses^{25,27,28}.

(4). Stress-corrosion cracking was for many years considered to require static stresses (see statement by Sutton et al.³ above). However, in 1961 Coleman et al.²⁹ demonstrated that stress-corrosion cracking could occur under conditions of dynamic loading in both an austenitic stainless steel

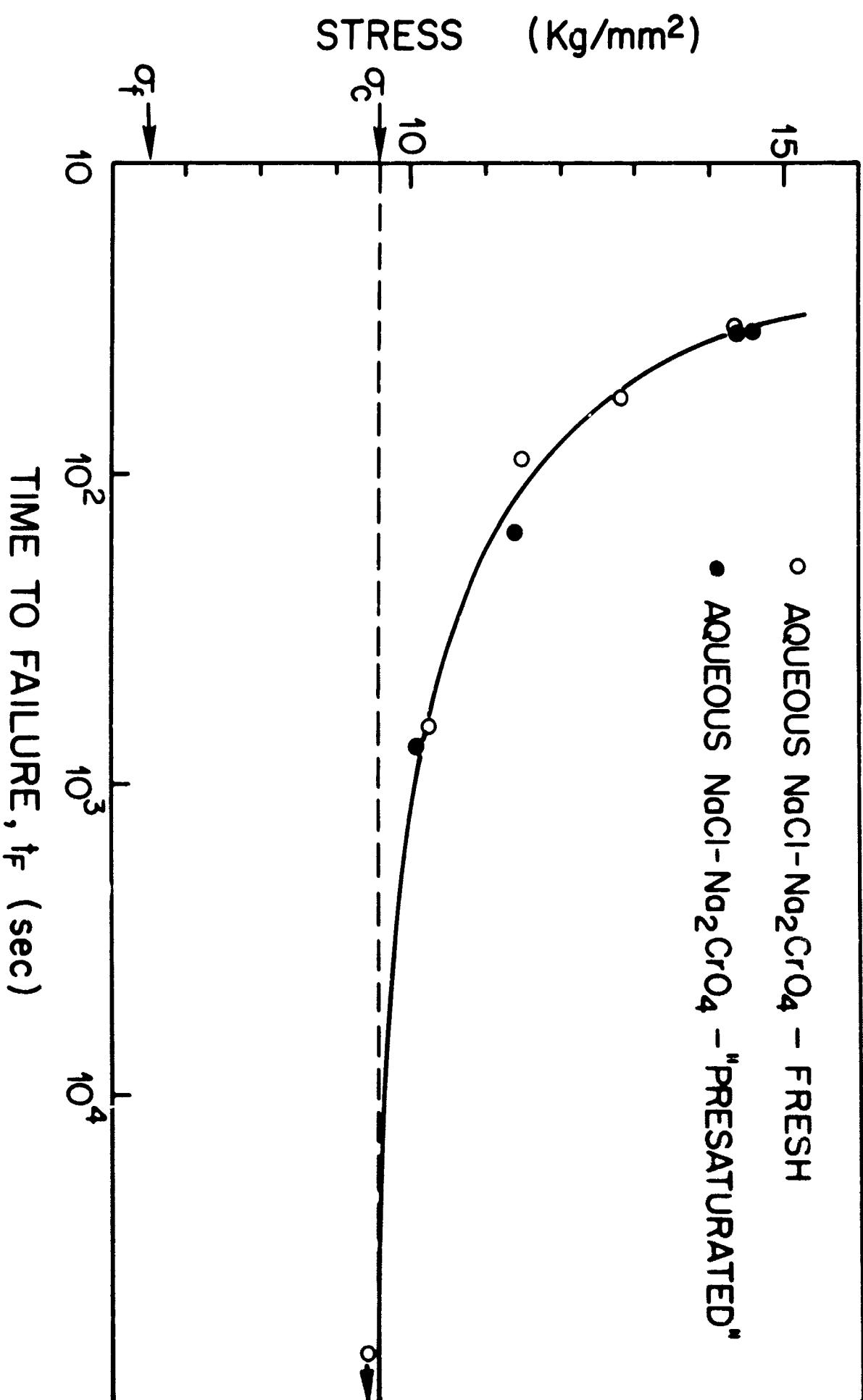


Fig. 1- Relationship between applied stress and time to failure for a commercial magnesium-aluminum alloy statically loaded in aqueous sodium chloride-sodium chromate solution. (Pugh et al.²³)

and in a magnesium-aluminum alloy. Since that time, similar results have been noted by other workers^{23,30,31}. Fig. 2 illustrates tensile stress-strain curves for a polycrystalline alloy containing 70 pct copper and 30 pct zinc stressed at a strain rate of ~ 5 pct/min in air and in oxygenated concentrated (~ 15N) aqueous ammonia containing 10 g/l copper, respectively²³. Failure in the ammoniacal environment was intercrystalline. Similar behavior was noted for all strain rates investigated (1 - 50 pct/min). Hoar and Scully³¹, investigating the effect of strain rate on the anodic dissolution rate of 18 pct Cr - 8 pct Ni stainless steel wires maintained at a constant potential, viz. - 0.14 v(e_H), in boiling 42 pct magnesium chloride solution, found that stress-corrosion cracking occurred at strain rates up to 13 pct/min but that at higher rates general dissolution took place, Table I.

In dynamic tests on a magnesium-base alloy and on α -brass, Fig. 2, stress-corrosion cracks were found to be initiated at stresses slightly above the flow stress, σ_f ²³. Coleman et al.²⁹ reported that in the austenitic stainless steel and the magnesium-aluminum alloy, cracking occurred at approximately the flow stress. Moreover, it was claimed that the stress to initiate cracks, σ_f , was dependent on the grain diameter, d . Plots of σ_f against $d^{-1/2}$ yielded straight lines, e.g. Fig. 3, and therefore it was suggested that the Petch-Stroh relationship^{32,33} was obeyed, that

$$\sigma_f = \sigma_0 + K d^{-1/2} \quad \dots \quad [1]$$

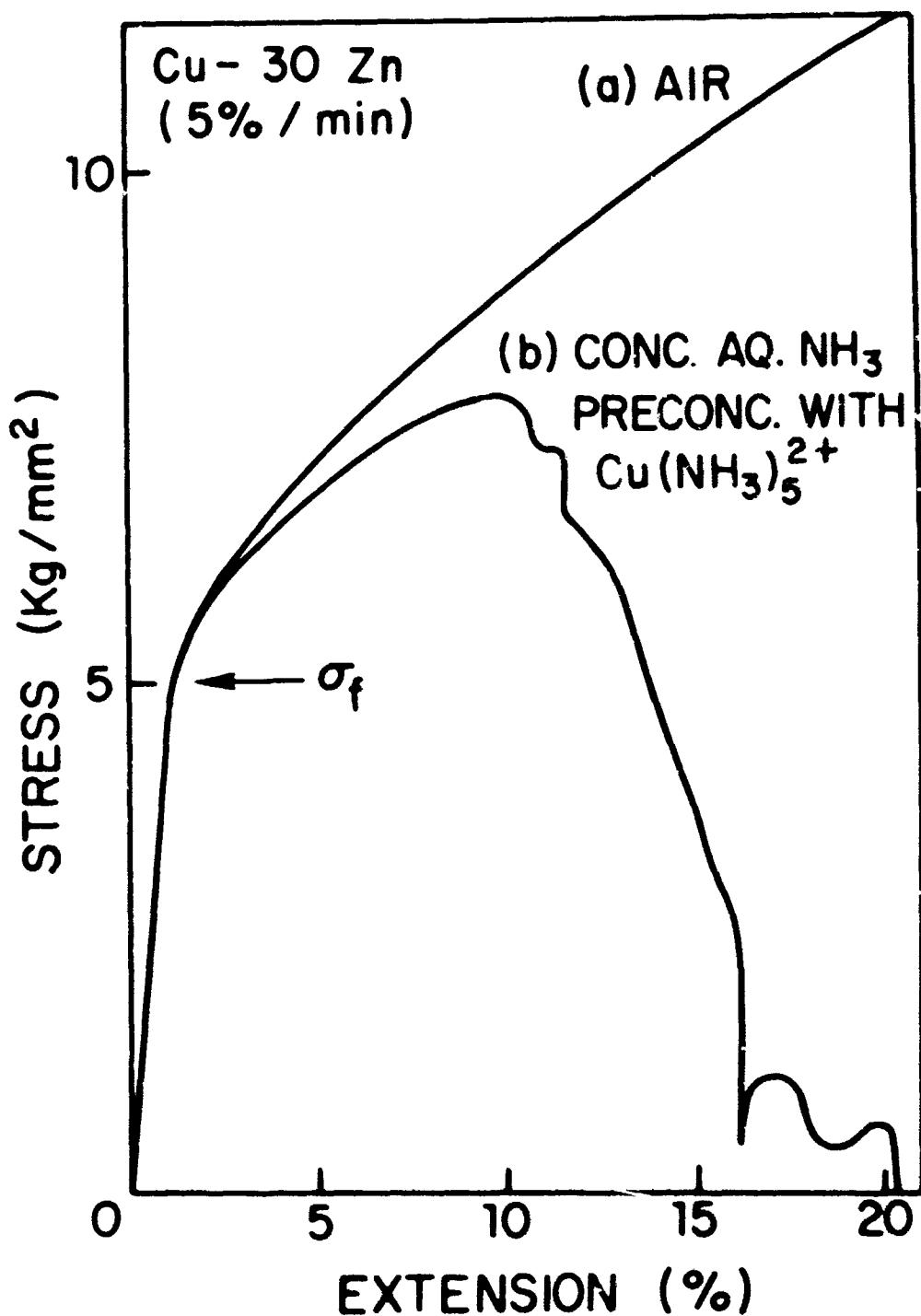


Fig. 2- Tensile stress-strain curve for Cu - 30 pct Zn alloy tested (a) in air and (b) in an aqueous ammoniacal solution containing a high concentration of Cu(NH₃)₅²⁺ ions. (Pugh et al.²³)

Table I. Influence of Strain Rate on Anode Current Density of 18 Cr-8 Ni Steel Wires held at -0.14v(e_H) in 42 pct. MgCl₂ at 154°C (after Hoar and Scully³¹)

	Strain Rate (pct/min)	Anode Current Density (ma/cm ²)
Stress-Corrosion	0	0.13
Cracking (about 400 cracks/ cm of wire)	4	0.24
	13	0.35
General	40	-
Dissolution	107	3.0

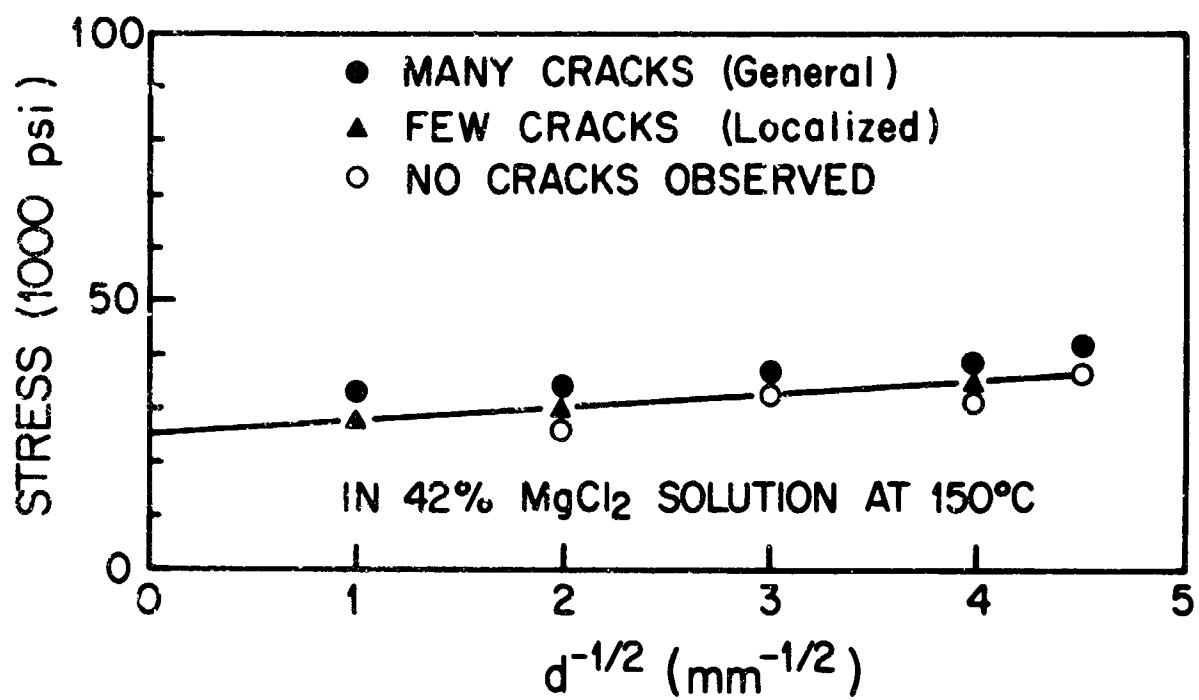


Fig. 3- Illustrating the relationship between the stress to initiate stress-corrosion cracks in 304 stainless steel and grain size, d . (After Coleman et al.²⁹)

where σ_0 and K are constants. Parkins¹⁴ has reported similar observations for mild steels stressed in boiling nitrate solutions. The significance of these observations is discussed below.

(5). It has been established that stress-corrosion cracking can be prevented by cathodic protection. This has been demonstrated for alloys of aluminum, copper, magnesium, and iron¹². It is widely considered that this indicates the fundamentally electrochemical nature of the stress-corrosion process, that the corrosion stage does not involve a homogeneous reaction in which the exchange of electrons between reacting species occurs locally, but rather an electrochemical reaction, where current flows over distances which are large on an atomic scale. This conclusion may be an oversimplification in some cases. For instance, cathodic protection prevents stress-corrosion cracking in α -brass stressed in oxygenated aqueous ammonia containing large concentrations of the cupric complex ion $\text{Cu}(\text{NH}_3)_5^{+2}$ ²³. However, it will be seen below that the mechanism of failure in such a solution is not electrochemical in the accepted sense. Moreover, the embrittlement of the non-metal silver chloride⁵⁻⁸ exhibits the phenomenological characteristics of stress-corrosion cracking. The likelihood of electron flow over relatively large distances in this material is remote.

Other characteristics have been suggested:

(6). It is widely held that stress-corrosion cracking is confined to alloys and that it does not occur in pure metals. While it is undoubtedly true that pure metals are far less susceptible than alloys, recent evidence suggests they are not completely immune. Thomas³⁴ has claimed to have produced

stress-corrosion cracking in quenched pure aluminum. Flis³⁵ has reported that whiskers of pure iron undergo intercrystalline stress-corrosion cracking in hot ammonium nitrate solutions. These reports remain to be confirmed; nevertheless, they indicate that this characteristic must be regarded with some caution.

(7). Several workers^{12,25, 36-38} have suggested that stress-corrosion behavior is related to the dislocation structure of the deformed material, which is related in turn to stacking-fault energy or to the presence of order in the material. Much of this work is recent and has not been extensively reviewed elsewhere, so that it is necessary to consider this topic in some detail.

In austenitic stainless steels, susceptibility to transcrystalline stress-corrosion cracking has been reported to be favored by the formation of planar dislocation arrays. Barnartt et al.³⁷ investigated a high-purity austenitic steel containing 16 pct chromium and 20 pct nickel. This material was found to be immune to stress-corrosion cracking in boiling aqueous magnesium chloride solution. The addition of 1.5 pct manganese produced no significant effect on stress-corrosion behavior, but additions of either 1.5 pct molybdenum or 0.5 pct titanium caused cracking to occur. Electron-microscope studies established that dislocations in the susceptible alloys formed planar arrays, while in the immune alloys a cellular dislocation distribution was produced. Moreover, measurements of stacking-fault energies, using the method described by Whelan³⁹, indicated that the energies were high for the immune materials

and low for the susceptible alloys, and it was concluded therefore that the formation of the planar arrays in the susceptible alloys resulted from the lowering of the stacking-fault energy so that cross glide was restricted.

Swann³⁸ has studied the effect of varying the nickel content of an austenitic steel containing 18 pct chromium. Earlier workers had established that increasing the nickel content above 8 pct results in an increasing resistance to stress-corrosion cracking,^{40,41} see Fig. 4. Using transmission electron microscopy, Swann found that increasing the nickel content caused an increase in stacking-fault energy, Fig. 4, accompanied by the expected changes in dislocation substructure (i.e. planar arrays to a more cellular distribution). However, Swann pointed out that the formation of planar dislocation arrays does not necessarily require low stacking-fault energies. For example, additions of either phosphorus or nitrogen were found to promote such arrays in these steels and also to reduce resistance to stress-corrosion cracking, but the stacking-fault energies remained high (see effect of nitrogen, Fig. 4). In these cases, Swann attributed the formation of planar arrays to ordering effects in the lattice. Both elements have a strong affinity for chromium so that it was suggested that they would be closely associated with chromium atoms in the austenite lattice. Dislocations moving through the lattice would destroy this relationship and enable subsequent dislocations on the same slip plane to glide more easily and hence form a planar distribution of dislocations.

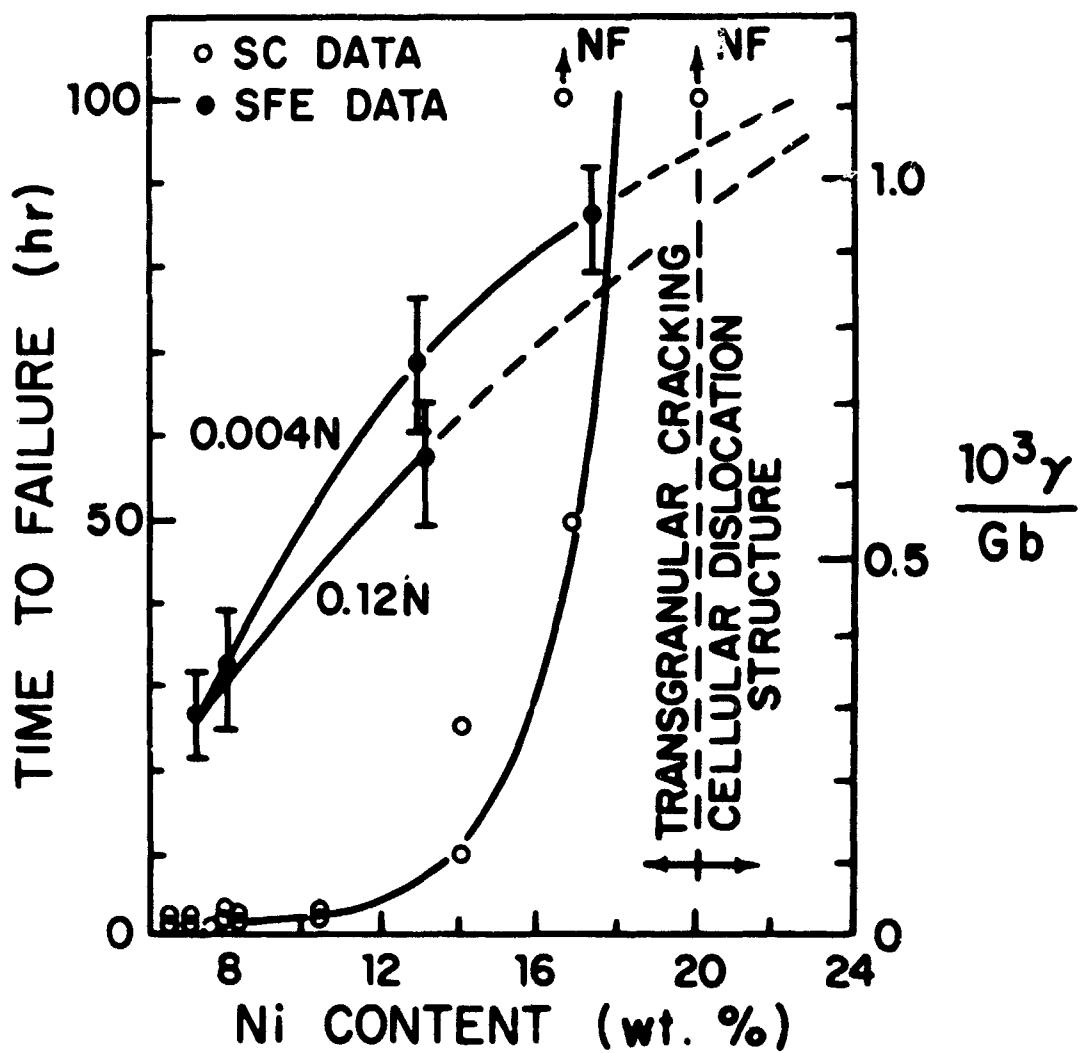


Fig. 4- Effect of nickel content on stacking-fault energy and time to stress-corrosion failure of ~ 18 pct chromium stainless steels. (After Swann³⁸.)

These observations suggest that the formation of planar dislocation arrays, caused either by low stacking-fault energy or by the existence of ordering, is a necessary condition for transcrystalline stress-corrosion cracking in austenitic stainless steels. However, recent work by Thomas, Stickler and Allio⁴² suggests that the formation of such arrays is not a sufficient condition, for it was found that while both 304 stainless steel (18 pct chromium and 8 pct nickel) and Incoloy 800, an austenitic alloy containing ~ 20 pct chromium and ~ 33 pct nickel, exhibit planar dislocation arrays, the former was highly susceptible to stress-corrosion cracking in boiling magnesium chloride solution while the latter was immune. More significantly, Saxena and Dodd⁴³ have reported that transcrystalline stress-corrosion cracking occurs in an austenitic stainless steel containing 20 pct chromium, 20 pct nickel, 1.5 pct molybdenum, and 0.3 pct carbon, despite the fact that cellular dislocation structures were observed; there was no evidence for the existence of planar arrays in the deformed material.

In copper-base alloys, it is accepted that stress-corrosion cracking can occur in materials in which dislocations form either planar arrays or cellular structures. For example, Thompson and Tracy⁴⁴ have reported stress-corrosion failures in a series of different binary alloys, including those with zinc, aluminum and phosphorus, respectively. Electron-microscope studies have shown that planar arrays exist in copper-zinc and copper-aluminum alloys, except for very dilute alloys⁴⁵, while cellular dislocation structures are formed in the case of copper-phosphorus alloys³⁶.

Several workers^{25, 36, 38} have suggested that the path of cracking in copper-base alloys is controlled by stacking-fault energy. Tromans and Nutting³⁶ have proposed that while intercrystalline cracking can occur in alloys of high or low stacking-fault energy, transcrystalline cracking is confined to the latter. According to these workers, cracking follows paths of highest dislocation density (the actual mechanism of failure is discussed in the following section). In materials of high stacking-fault energy, grain boundaries were considered to constitute regions of high dislocation density, so that intercrystalline cracking was predicted; easy cross-glide in such materials prevents the formation of stable dislocation pile-ups within the grains and therefore the theory indicates that no transcrystalline cracking should occur. Tromans and Nutting suggested that in the case of materials of low stacking-fault energy, the path of cracking depends on the amount of plastic strain. At low strains, dislocation pile-ups are confined largely to grain boundaries, while at higher strains pile-ups also occur within the grains. It was predicted, therefore, that cracking would be intercrystalline at low strains, and both inter- and transcrystalline at higher strains.

These predictions are supported, to some extent, by experimental observations. There is no evidence in the literature that transcrystalline stress-corrosion cracking occurs in copper alloys of high stacking-fault energy. Moreover, the proposed strain-dependent transition from inter- to transcrystalline cracking has been observed in 70:30 brass (low stacking-fault energy, ~ 8 ergs/cm²)^{36, 46}. The results reported by Swann³⁸ are of particular

interest. It was considered that the transition in copper-zinc alloys corresponds simply to the change from a cellular dislocation structure (high stacking-fault energy) to one exhibiting planar dislocation arrays (low stacking-fault energy). This conclusion was based on a comparison of stress-corrosion data reported by Robertson and Tetelman²⁵, the stacking-fault energies of Howie and Swann⁴⁷, and electron-microscope studies by Swann³⁸, see Fig. 5. The stress-corrosion results were obtained from copper-zinc alloys prestrained 37 pct, and tested in ammonia vapor under an applied stress of 25 pct of that required to produce 37 pct strain in each alloy. Under these conditions, the transition from intercrystalline to transcrystalline cracking was observed to commence at 18 pct zinc. The electron-microscope studies, carried out on alloys strained 5 pct, indicated that the transition from cellular dislocation structures to planar arrays also occurred at ~ 18 pct zinc, Fig. 5. However, this correlation presumably results from the particular stress-corrosion testing procedure, the use of the large prestrains ensuring the formation of pile-ups within the grains of alloys of low stacking-fault energies. Such a correlation would not be expected under different testing conditions. Indeed, Robertson and Tetelman²⁵ emphasized that the transition in the mode of cracking depends on the amount of plastic prestrain.

Data for copper-aluminum alloys also are presented in Fig. 5. It must be pointed out that in this case the transition from inter- to transcrystalline cracking is simply a prediction by Swann³⁸ based on his electron-microscope studies. There are no experimental data in the literature concerning the transition composition, if such exists.

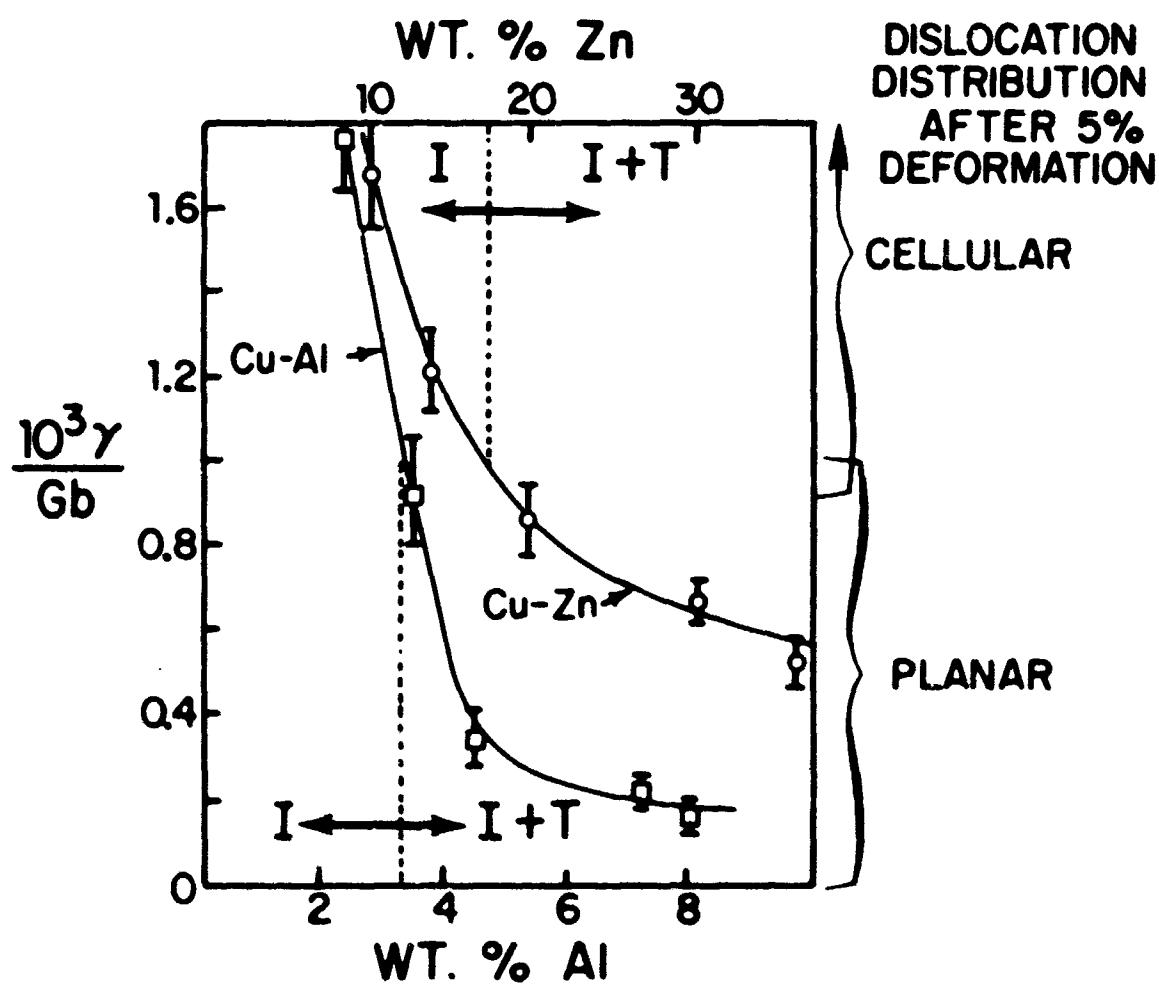


Fig. 5- Relationship between stacking-fault energy γ (in units of 10^{-3} Gb), dislocation structure, and mode of stress-corrosion failure for copper-zinc and copper-aluminum alloys. The broken lines are claimed to indicate the transition from intercrystalline (I) to transcrystalline (T) cracking.
(After Swann³⁸.)

To summarize, the earlier suggestion^{37, 38} that transcrystalline stress-corrosion cracking in austenitic stainless steel occurs only in alloys in which planar dislocation arrays are formed has not been confirmed by later studies. Thomas et al.⁴² have shown that the formation of planar arrays is not a sufficient condition for cracking to occur, and more recent work by Saxena and Dodd⁴³ has indicated that such arrays are not a necessary condition. In the case of copper-base alloys, the existing evidence suggests that transcrystalline cracking is confined to materials of low stacking-fault energy (i.e. those in which planar arrays are formed). However, the relevance of dislocation structure in copper alloys can be questioned, since it has been shown that either trans- or intercrystalline cracking can be produced in an alloy containing ~ 37 pct zinc by varying the pH of the environment¹⁶.

PROPOSED MECHANISMS

The electrochemical theory proposed by Dix and his coworkers^{4, 48} serves as a useful introduction. According to this generalized model, a prerequisite for stress-corrosion cracking is the existence of a localized anodic path in the material. Thus in the presence of a corrosive aqueous environment and a tensile stress, a galvanic cell is set up in which the anodic path is preferentially attacked. The base of the resulting corrosion crevice then becomes the site of stress concentrations, and these were thought to cause the metal to "tear apart by mechanical action". It was considered

that the "tearing action" exposes fresh metal, unprotected by films, so that accelerated corrosion occurs in this region. This in turn leads to further stress concentration and further "tearing" of the metal. Thus cracking propagates by cycles of accelerated corrosion and "tearing" of the metal.

While this model accounted for the apparent electrochemical nature of stress-corrosion cracking, it left many questions unanswered, principally concerning the phrase "tearing apart by mechanical action". Later workers interpreted this phrase differently. For example, Uhlig⁴⁹ considered that it referred to plastic deformation of the substrate, which destroys protective films and thereby continually exposes fresh anodic material to the environment. On the other hand, Harwood²⁴ argued that the phrase implied a stage of brittle mechanical fracture of the metal itself. These viewpoints clearly are diametrically opposed. According to the former, crack propagation proceeds by preferential dissolution at the crack tip, while according to the latter cracking is mechanical. It would appear that this question could be readily resolved by studies of crack propagation, but unfortunately it is difficult to interpret the results of such studies unambiguously. In fact, this dichotomy still exists -- the many theories which have been proposed since the early theory of Dix et al. fall into two main groups: (i) those which consider cracking proceeds by preferential dissolution, (ii) those which consider that cracking is mechanical.

Consider the main problems faced by the two groups. Proponents of the dissolution theory have to explain how dissolution is concentrated at the crack tip and have to account for the high rates of cracking commonly observed. For example, it has been claimed that a characteristic cracking rate* of 1 cm/hr exists for many stress-corrosion systems⁵⁰; this rate is thought to be considerably higher than normal corrosion rates³⁸. On the other hand, any mechanical model must account for the occurrence of brittle failures in normally ductile materials. Contrary to the statement of Robertson and Tetelman²⁵, concerning the intercrystalline stress-corrosion cracking of homogeneous fcc alloys, that "it is not hard to imagine that the (corroding) boundary can be weakened so that small stress concentrations at the boundary can provide the energy to cause fracture", it is in fact difficult to explain in detail how failure occurs. Harwood²⁴, for example, has suggested that plastic deformation at the tip of the corrosion crevice produces "conditions of constraint and multiaxial stresses" which in turn lead to brittle cracking. However, it is difficult to reconcile this model with the behavior of materials such as austenitic stainless steel and α -brass which show no notch sensitivity in the absence of the embrittling species. This criticism can also be levelled against the more recent suggestion by Nielsen⁵¹ that the deposition of solid corrosion products within a corrosive crevice in austenitic stainless steel can assist in producing stress-corrosion

* The reliability of measured rates of cracking is questionable because in many systems it is not known whether cracking is continuous or discontinuous.

cracking by exerting a wedging action. This might in fact make some contribution to the stress concentration, but in no way explains how this stress leads to brittle fracture rather than to plastic deformation.

In the following pages, some of the specific models are described and correlated with experimental findings.

Dissolution Models: Any model of stress-corrosion cracking must account for both crack initiation and crack propagation. In general terms, the initiation stage presents little difficulty, since the formation of a corrosion crevice, possibly of microscopic dimensions, can be imagined to occur by several processes, e.g. preferential dissolution at grain boundaries, stacking faults, and/or slip bands. The major problem facing dissolution models, as we have seen, is to explain how further dissolution is concentrated first at the tip of the crevice, allowing it to grow into a macroscopic crack, and then at the crack tip itself. Since plastic deformation is concentrated ahead of the crevice or crack, it would be attractive to attribute the rapid dissolution to the higher energy of the deformed material, that is, to the fact that deformed metal is anodic relative to undeformed metal. However, it is generally considered that the effect of elastic strain energy is too small to account for a significant increase in dissolution rate^{12,49}.

It has been suggested that preferential dissolution occurs at the tip of the crevice because plastic deformation, concentrated in that region, causes the rupture of passive surface films⁵²⁻⁵⁴. A galvanic cell is thus set up

between the film-free region at the tip of the crevice (anodic) and the filmed sides of the crevice (cathodic). Dissolution at the tip leads to further stress concentration and hence to further localized plastic deformation, which in turn prevents the reformation of the passive film in that region and thus ensures further localized dissolution. Cracking then proceeds by repeated cycles of deformation and dissolution. Film-rupture mechanisms of this type have been advocated by Champion⁵² and Logan^{53,54}. The mechanism is similar to that of Dix et al.^{4,48} but it differs from the latter in that it does not imply any stage of mechanical cracking of the metal itself. Moreover, it does not require a pre-existing anodic path.

A criticism of the film-rupture model was that it does not account for the absence of marked susceptibility to stress-corrosion cracking in pure metals, which also become coated with passivating films. This objection has been met by recent developments of the film-rupture mechanism, notably by Swann and Embury⁵⁵. These workers, considering transcrystalline stress-corrosion cracking, argue that surface films are more likely to be ruptured by coarse than by fine slip. The height of slip steps in pure metals and dilute alloys is small and therefore it was considered that film rupture is unlikely. On the other hand, alloys of low stacking-fault energy or alloys in which ordering exists, exhibit coarse slip and in these materials film rupture can be expected. This argument thus predicts a correlation between susceptibility to transcrystalline stress-corrosion cracking and coarse slip (i.e.

planar dislocation arrays). It was seen above that there is meager evidence for such a correlation.

The film-rupture model for transcrystalline stress-corrosion cracking, as modified by Swann and Embury⁵⁵, can be summarized as follows:^{*}

- (i) Formation of a passive film over most of the surface.
- (ii) Rupture of the film by slip.
- (iii) Tunnel corrosion at the exposed metal, leading to the formation of tubular corrosion pits. Pits of this type have been observed by Pickering and Swann⁵⁶ in several alloys, viz. copper-zinc, copper-aluminum, and magnesium-aluminum alloys, after exposure to solutions which cause stress-corrosion cracking. Nielsen⁵⁷ has reported a similar type of tunnel corrosion in austenitic stainless steels exposed to boiling aqueous magnesium chloride solutions.
- (iv) Ductile rupture of a slot weakened by many tubular pits.

This model is illustrated schematically in Fig. 6. It differs from the earlier film-rupture theories⁵²⁻⁵⁴ in that it involves tunnel corrosion and stages of ductile fracture of the metal itself.

The cause of tunnel corrosion is not fully understood. Nielsen⁵⁷ suggested that the tunnels in stainless steels may form by corrosion along Lomer-Cottrell dislocations, narrow stacking-fault ribbons, or alpha ferrite needles. The first two of these possibilities seems unlikely in view of the observations by Swann and his colleagues that dislocations within the slip

* This model was developed from earlier mechanisms proposed by Swann⁵⁸, and by Pickering and Swann⁵⁶.

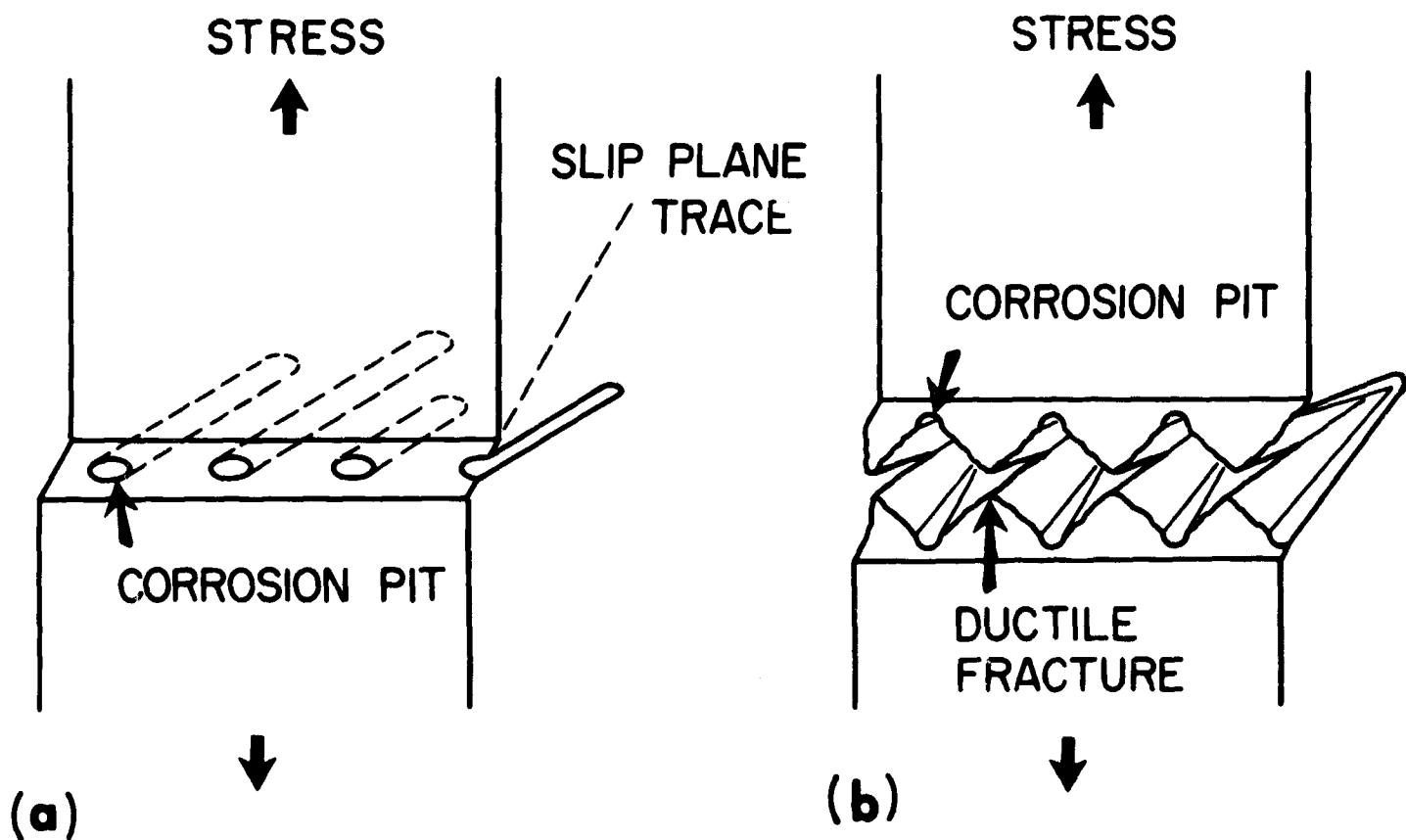


Fig. 6- Schematic representation of film-rupture mechanism for stress-corrosion cracking. (a) Pits are initiated at areas where surface films have been ruptured by slip. Under suitable conditions the pits grow into tubular tunnels. (b) Rupture occurs along a plane containing the corrosion tunnels. (After Swann and Embury⁵⁵.)

band are not favored sites for initiation of the tunnels⁵⁵, and that the tunnels do not necessarily follow slip planes⁵⁶. Westwood⁵⁸ has pointed out that similar tunnels have been found in lithium fluoride following immersion in water containing a strongly-adsorbing step-poison, e.g. fatty acid molecules⁵⁹ or ferric fluoride complexes⁶⁰; tunneling was not observed in the absence of such poisons. It was suggested, therefore, that the presence in solution of certain strongly adsorbing species may be responsible for the tunneling found in materials exposed to environments which cause stress-corrosion cracking. In this connection, it is interesting to note that the chloride ion has been found to be strongly adsorbed on surfaces of austenitic stainless steel⁶¹.

An alternative dissolution model has been proposed by Hoar and Hines⁶², based on the concept of mechanochemical anodic dissolution. According to this approach, anodic dissolution is directly assisted by continuous plastic deformation. Thus yielding at the tip of a corrosion crevice is thought to cause preferential dissolution in that region, and, as in the film-rupture model, this causes further localized deformation. In this case, cracking then proceeds by continuous yielding and localized dissolution at the crack tip. Later work by Hoar and his colleagues^{30,31} has been claimed to provide evidence for the mechanochemical effect. For example, Hoar and Scully³¹ have investigated the effect of continuous yielding on the dissolution behavior of wires of 18 pct chromium, 8 pct nickel stainless steel in boiling 42 pct aqueous magnesium chloride solution, maintained at a constant potential by means of a potentiostat. The anode current density was found to

increase significantly with increasing strain rate, Table I, indicating that yielding causes increased rates of anodic dissolution

The mechanism of the proposed mechanochemical effect has not been explained, although it has been suggested that the arrival of dislocations increases the number of anodically active sites by disarraying the surface⁵¹. It was further suggested that this effect would be greater in materials which show restricted slip (i.e. materials exhibiting planar dislocation arrays) than in those which can cross slip readily. This argument would appear debatable, since many small slip steps might be imagined to provide a greater number of active sites than several large steps.

The film-rupture model and the mechanism based on mechanochemical anodic dissolution can be seen to display several common features. In particular, both are considered by their advocates to be operative in austenitic stainless steels undergoing stress-corrosion cracking in boiling 42 pct aqueous magnesium chloride solutions. It is interesting that the results of Hoar and Scully⁵¹, Table I, presented as evidence for the mechanochemical model, would also appear to be consistent with the film-rupture mechanism -- increasing strain rates would be expected to lead to increasing damage to surface films and hence to increasing anodic dissolution. However, it is commonly claimed, on the basis of electrode-potential studies, that passivating films are not formed on stainless steel in aqueous magnesium chloride, particularly in solutions acidified by the addition of small amounts of hydrochloric acid^{62,63}. On the other hand, recent metallographic evidence by Swann and Embury⁵², using a platinum decorating technique⁵⁷,

suggests that a film is formed and, moreover, that it is ruptured by plastic deformation of the substrate. It is clear that further work is necessary to clarify the role of surface films in this system.

The final dissolution model to be considered involves the suggestion that solute atoms segregate to dislocations created during stressing, thus causing preferential attack at these defects^{36,49}. This approach has been developed by Tromans and Nutting³⁶, who pointed out that the path of cracking would therefore be expected to depend on the dislocation structure of the stressed material. This model was discussed above, where it was seen that it accounts to some extent for observations on the path of cracking in copper alloys. Tromans and Nutting proposed that cracking occurs primarily by a single-stage mechanism involving a rapid rate of chemical attack at dislocations, and the linking of these corrosion sites to form macrocracks. However, it could be argued that the theory is essentially one for crack initiation, since it leaves many questions unanswered concerning crack propagation.

In summary, then, the main dissolution models are:

- (1). The film-rupture theory.
- (2). The theory involving the concept of mechanochemical anodic dissolution.
- (3). The theory based on preferential dissolution at "decorated" dislocations.

Mechanical Models: It was seen above that the major problem faced by mechanical models is to explain how the presence of a corrosive environment causes cracking in normally ductile materials. Age-hardening aluminum alloys

represent a special case because they possess an inherent structural weakness. Preferential grain-boundary precipitation during aging leads to the formation of precipitate-free zones at the boundaries in these alloys, Fig. 7⁶⁴. The zones are mechanically weak compared to the solid solution within the grains so that upon stressing they become the sites for preferential deformation. Thomas and Nutting⁶⁴ have suggested that grain-boundary deformation plays an important role in stress-corrosion cracking, although the process was not discussed in detail.

Pugh and Jones⁶⁵ have considered the stress-corrosion cracking of a high-purity aluminum alloy containing 5.5 pct zinc and 2.5 pct magnesium. Studies of the surfaces of aged specimens undergoing stress-corrosion cracking in moist air indicated that the first stage in the process was the formation of continuous paths of grain-boundary deformation, Fig. 8, perpendicular to the tensile axis. The grain-boundary paths illustrated in Fig. 8 appear dark and well-defined because of severe surface rumpling at the boundaries caused by deformation within the precipitate-free zones; no cracks were present. The length of the paths, and the amount of deformation in the neighboring grains, was observed to increase with time. Fracture finally occurred over an intercrystalline path which included a deformed path. The significant feature of these observations was that no cracks were detected along the deformed paths before final fracture. It was considered, therefore, that cracking occurred by rapid, mechanical fracture.



Fig. 7- Transmission electron micrograph illustrating the precipitate-free zones at grain boundaries in an aged aluminum-zinc-magnesium alloy.
(After Thomas and Nutting⁶⁴.)



Fig. 8- Illustrating paths of grain-boundary deformation in an aged aluminum-zinc-magnesium alloy statically stressed in moist air for 3 days (above) and 6 days (below), respectively. The specimens were electro-polished before testing; the intercrystalline paths appear dark because of localized surface deformation at those grain boundaries. Bright field. (Pugh and Jones⁶⁵.)

The following mechanism was proposed to explain these observations:

Grain boundaries in alloys of this type are known to be anodic relative to the grains, and it is thought that exposure to corrosive environments leads to localized attack at grain boundaries, forming corrosion crevices^{4,48}. In the presence of tensile stresses, stress concentrations set up at the extremities of these crevices are relieved by plastic deformation within the precipitate-free zones. The preferential deformation in turn ruptures protective (oxide) films in the grain boundary region, leading to further localized corrosive attack. In this way, cycles of localized corrosion and deformation occur at certain grain boundaries. Moreover, corrosion crevices near the extremities of the initial paths of deformation create stress-concentrations which are relieved by plastic deformation in the adjoining, previously undeformed precipitate-free zones, thus causing the growth of the deformed path. At the same time, repeated cycles of corrosion and preferential deformation along the path result in hardening and eventual crack initiation. In the coarse-grained specimens (4 grains/mm²) used in these experiments, the initial crack propagated catastrophically through the grain-boundary zones. This would not be the case in material of finer grain size, in which several cycles of grain-boundary creep and mechanical fracture would be expected.

The studies of Pugh and Jones⁶⁵ were confined to high-purity alloys containing zinc and magnesium. However, precipitate-free zones are known to exist in other age-hardening aluminum alloys⁶⁴, and there is evidence that crack propagation is mechanical in these alloys^{66,67}. Therefore, it is considered likely that the same mechanism is operative.

While the mechanism outlined above accounts for many characteristics of stress-corrosion failure in aluminum alloys, several aspects of the process require further study. For example, the stress-corrosion life of age-hardening aluminum alloys is known to decrease with increasing aging time to a minimum value, after which it progressively increases^{68,69} (see Fig. 9⁶⁹). It has been claimed that minimum life occurs at maximum hardness, because the difference in hardness between the grains and the precipitate-free zones is thought to be greatest at this stage^{14,64}. However, studies of high-purity alloys containing 5.5 pct zinc, 2.5 pct magnesium, and separate additions of small amounts of either copper, manganese, chromium, silicon, or iron, have indicated that minimum life occurs considerably earlier in the aging process than peak hardness⁶⁹. A typical relationship between stress-corrosion life and hardness is illustrated in Fig. 9. No explanation has been put forward relating the minimum life with structural changes during aging.

A second area requiring further attention concerns the nature of the fracture surfaces. According to the proposed mechanism, crack propagation is purely mechanical. Brittle intercrystalline fracture also can be produced in alloys of this type in conventional tensile tests, and in these instances the fracture surfaces are characterized by a dimpled pattern, thought to result from plastic deformation in the precipitate-free zones ahead of the advancing crack⁷⁰. It would be expected, on the basis of the preceding model, that fracture surfaces produced during stress-corrosion cracking would show a similar structure. However, fractographic studies by Forsyth and Ryder⁷⁰, carried out on a stress-corroded commercial aluminum-zinc-magnesium alloy, have indicated that two distinct types of intercrystalline

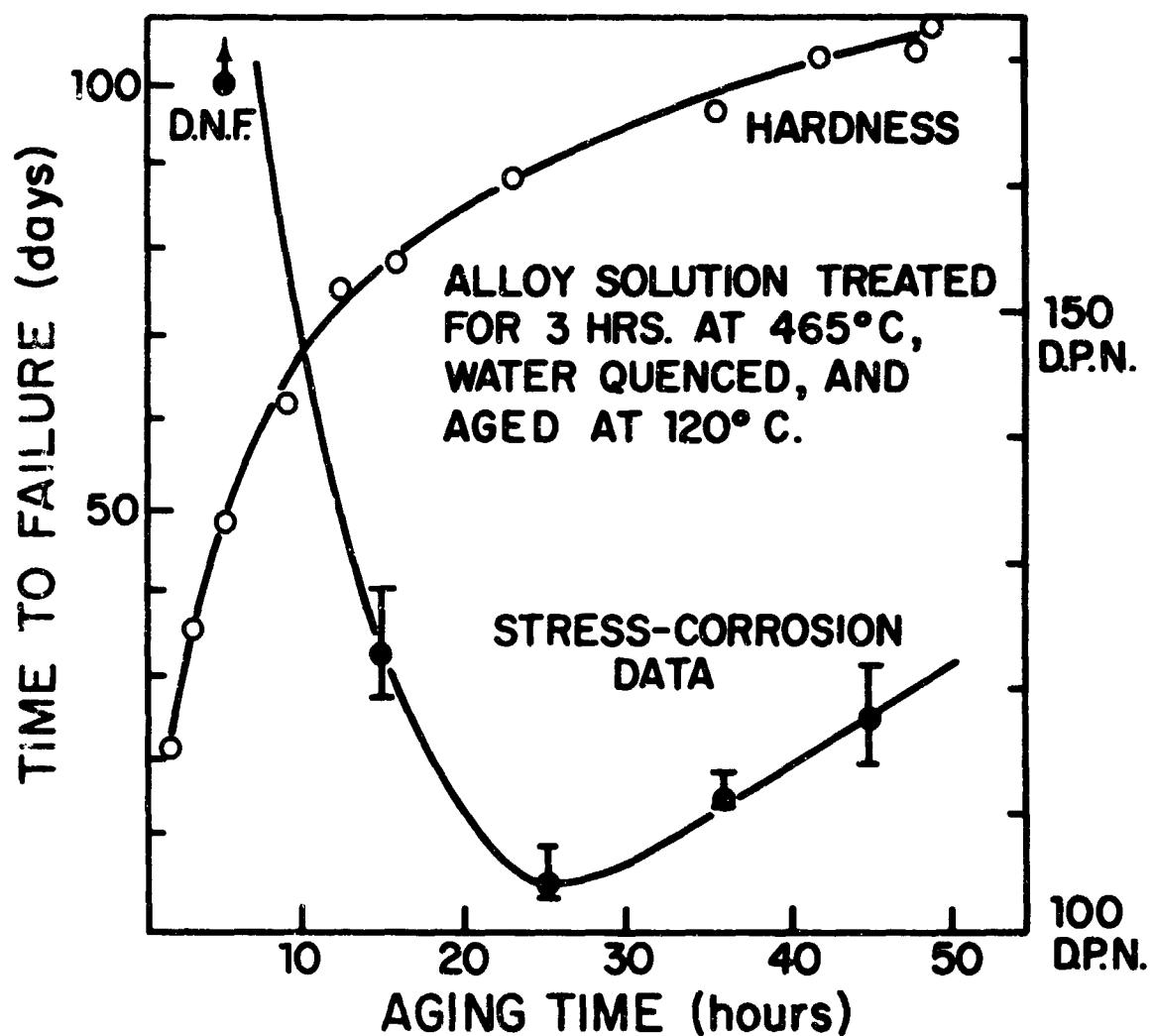


Fig. 9- Effect of aging time on hardness, and on stress-corrosion life for a high-purity aluminum alloy containing 5.5 pct zinc, 2.5 pct magnesium, and 0.2 pct iron. (Pugh⁶⁹.)

fracture surface exist. One type was found to exhibit the dimpled pattern, but in the other case the surfaces were smooth, indicating that cracking was accompanied by little plastic deformation. It is possible that the smooth surfaces correspond to the initial stages of fracture through the severely work hardened grain-boundary zones, and that the dimples occur when the crack enters previously undeformed regions. However, further metallographic studies are necessary to confirm this.

It is clear that the mechanism outlined for aluminum alloys cannot be applied to the more general case of inherently ductile single-phase materials such as α -brass and austenitic stainless steels. Several workers^{29,49,71} have suggested that stress-corrosion cracking in such cases may result from the adsorption of specific ion species. Following the approach used by Petch in his theory for the hydrogen embrittlement of steels^{72,73}, Coleman et al.²⁹ proposed that the role of adsorption is to lower surface energy. According to the Petch-Stroh relationship (see above),

$$\sigma_F = \sigma_0 + K d^{-1/2} \quad \dots \quad [1]$$

where σ_F is the stress required to cause brittle fracture, d is the average grain diameter, and σ_0 and K are constants. In particular,

$$K = \left(\frac{6\pi G\gamma}{1-\nu} \right)^{1/2} \quad \dots \quad [2]$$

where G is modulus of rigidity, ν Poisson's ratio, and γ the surface energy associated with the formation of new surfaces by fracture. Thus, for constant grain size, it follows that if γ is reduced by any process, then α_p also will be reduced.

Coleman et al. determined the stress necessary to initiate stress-corrosion cracks as a function of grain diameter, d , for both a magnesium-6 pct aluminum alloy in a sodium chloride-potassium chromate solution, and for an 18-8 austenitic stainless steel in aqueous magnesium chloride solution. The relationships between the stress and $d^{-1/2}$ were claimed to be linear in both cases, e.g. Fig. 3. From the slope of these relationships and from Eq. [2], γ was found to be 93 ergs/cm^2 for the magnesium-base alloy, and 157 ergs/cm^2 for the steel. These values are considerably lower than estimates of the true surface energies for these materials, ~ 500 and $\sim 1000 \text{ ergs/cm}^2$, respectively. It was considered that the reduction in γ was due to adsorption, and that this reduction allowed brittle failure to occur in these materials.

This conclusion can be questioned from two standpoints. First, it can be argued that the data do not provide convincing evidence that the Petch-Stroh relationship is obeyed, since the grain-size dependence, if it exists, is extremely small (see Fig. 3). Second, if it is accepted that this relationship is in fact obeyed, then the meaning of the surface energy term, γ , can be questioned⁷⁴. It would appear that this term should more properly represent the total energy involved in the creation of new surfaces,

thus including such terms as the surface free energy, the energy expended by plastic deformation, and the chemical energy supplied by the environment. The relative contribution of these terms to the total energy is a matter for speculation. Thus, viewed in this light, the claim that embrittlement results from an adsorption-induced reduction in surface free energy clearly remains to be demonstrated.

The surface-energy mechanism also can be criticized on the grounds that it does not explain the specific nature of the environments which cause stress-corrosion cracking, nor does it account for the relative immunity of pure metals to this failure. Furthermore, the surface-energy approach, which has also been put forward to explain liquid-metal embrittlement⁷⁵, has been criticized because it does not give any insight into the mechanism of failure on an atomic scale^{13,76}. More recently, an alternative adsorption-dependent mechanism has been proposed for liquid metal embrittlement, according to which embrittlement results from the adsorption and interaction of specific species with strained bonds, causing a localized reduction in cohesive strength^{13,76,77}. In addition, recent work has suggested that the embrittlement of the non-metal silver chloride in certain aqueous solutions occurs by a similar adsorption-dependent mechanism⁵⁻⁸.

The embrittlement of silver chloride is of particular interest because it displays many of the phenomenological characteristics of stress-corrosion cracking in metals:

- (i) Fracture of polycrystals stressed in air is ductile and transcrystalline, but becomes brittle and intercrystalline when the tests are conducted in certain aqueous environments⁵⁻⁸.

(ii) In tests under constant load, the relationship between time to failure,

t_y , and the stress level is similar to that for metals undergoing stress-corrosion cracking, cf. curve A, Fig. 10⁵ and Fig. 1.

(iii) Environments which cause embrittlement are specific. In each case, dissolution of the specimens in embrittling solutions leads to the formation of silver complex ions, Table II. Complex ions in solutions which cause cracking can have different structures and can be either positively or negatively charged, but the magnitude of the charge must be high, $> 1^+$ and $> 2^-$, Table II^{6,7}.

It has been proposed that cracking in silver chloride results from the adsorption of highly charged complex ions at regions of stress concentration⁶⁻⁸. For example, intercrystalline cracks are commonly initiated when slip bands are arrested at grain boundaries of large misorientation, Fig. 11(a); on the other hand, cracking is not observed at boundaries where the stress fields associated with the blocked slip bands are relieved by slip in the neighboring grain, Fig. 11(b)⁷. Once a crack is formed, the tip itself becomes a region of stress concentration. It was suggested that adsorption of the complex ions at strained bonds perturbs the distribution of bonding electrons*, reducing bond strength and hence allowing rupture at reduced stress levels.

Embrittlement in silver chloride was considered to result from adsorption rather than from, say, stress-dependent dissolution for several reasons:

* Bonding in silver chloride is thought to be 70 pct covalent and 30 pct ionic⁷⁸.

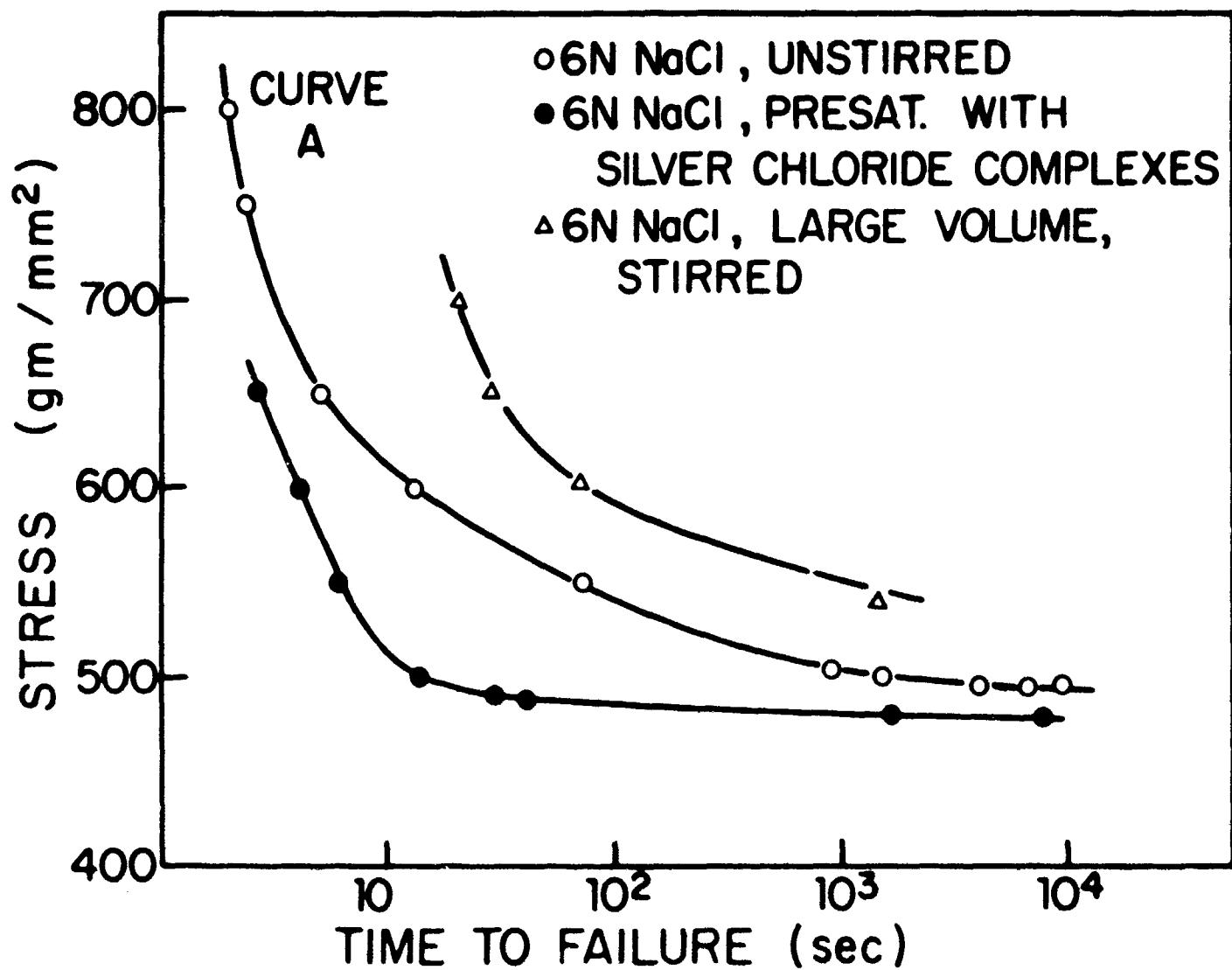


Fig. 10- Effect of applied stress on the time to failure of polycrystalline silver chloride stressed in 6N aqueous sodium chloride solutions at room temperature. (Westwood et al.⁵)

Table II. The Relationship between the Charge on Silver Complex Ions and their Ability to Embrittle Polycrystalline Silver Chloride (after Westwood et al.^{6,7}).

SOLUTION	PREDOMINANT COMPLEX ION	CHARGE	EMBRITTLEMENT
10N NH ₄ OH	Ag(NH ₃) ₂ ⁺	1+	NO
< 0.1N AgNO ₃	Ag ₂ Cl ⁺	"	"
0.1N NaCl	AgCl ₂ ⁻	1-	"
1N NaCl	AgCl ₃ ²⁻	2-	"
11N CsCl	(AgCl ₄) _m Cs ⁿ⁺	< 3-	"
5.8N KCl	(AgCl ₄) _m K ⁿ⁺	"	"
17N AgNO ₃	Ag ₃ Cl ²⁺	2+	YES
6N NaCl	AgCl ₄ ³⁻	3-	"
11.8N HCl	"	"	"
13.8N LiCl	"	"	"
8N NaBr	AgBr ₄ ³⁻	"	"
20N LiBr	"	"	"
17N NaSCN	Ag(SCN) ₄ ²⁻	"	"
6N Na ₂ S ₂ O ₃	Ag(S ₂ O ₃) ₃ ⁵⁻	5-	"

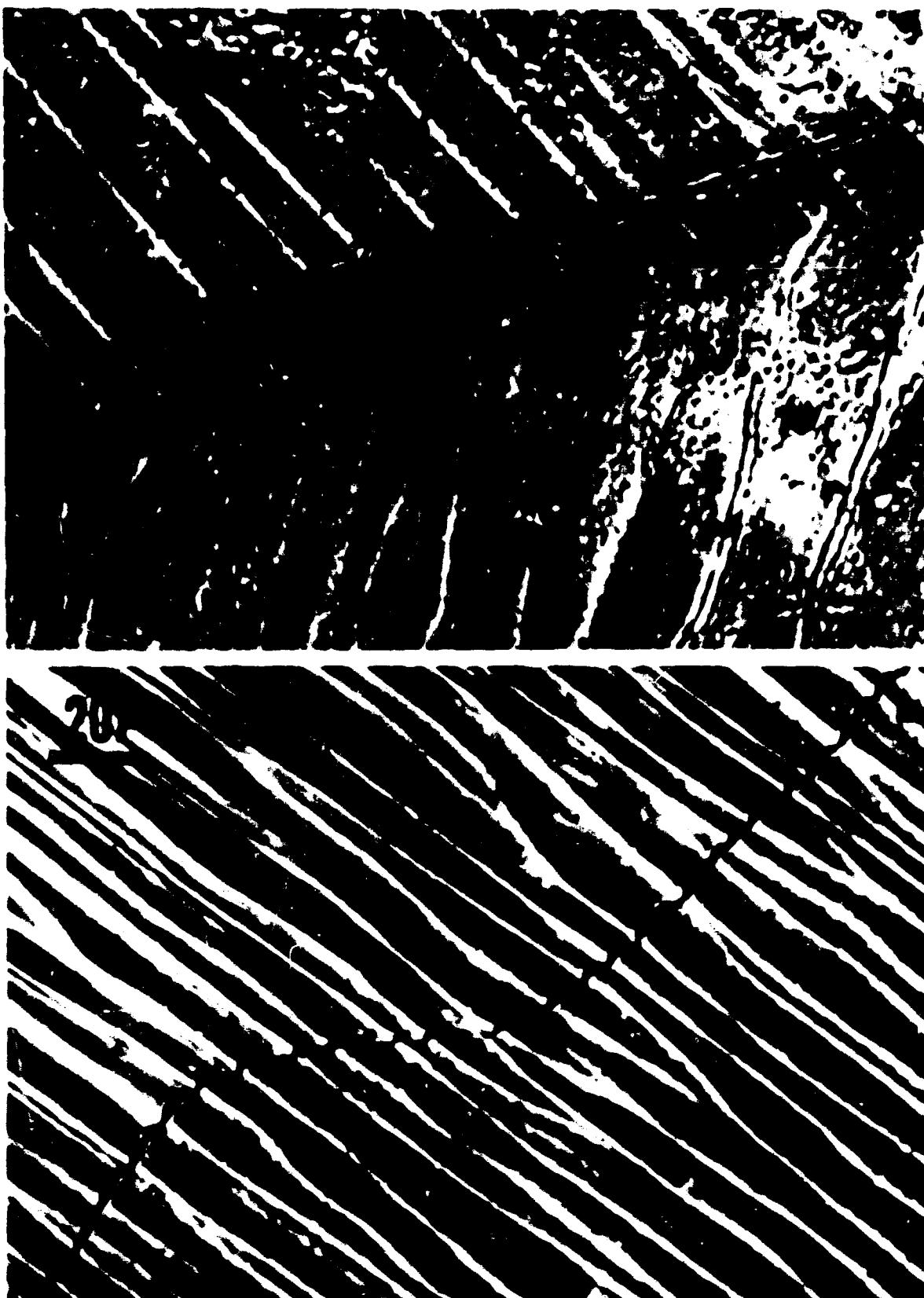


Fig. 11- Specimen of polycrystalline silver chloride deformed in 6N sodium chloride solutions presaturated with AgCl_4^{3-} ions. (a) Cracks are initiated where slip is arrested by a grain boundary of suitably large misorientation. (b) Cracks are not formed when the boundary is such that stress-concentrations associated with arrested slip bands are relieved by slip in the neighboring grain. Transmitted light. (Westwood et al.⁷)

(i) t_F was observed to decrease markedly when the testing solutions were presaturated with the silver complex ions before testing, Fig. 10⁵.

Similarly, t_F for specimens tested in "unpresaturated" solutions increased when the volume of the test solution was increased, Fig. 10; this was attributed to the fact that longer times were then required to produce a sufficient complex-ion concentration to cause cracking⁵.

(ii) Embrittlement did not occur in potassium chloride solutions⁶, despite the fact that the solubility of silver chloride in these solutions is virtually the same as that in sodium chloride solutions of the same Cl⁻ ion concentration⁷⁹ (sodium chloride is highly embrittling, see Fig. 10). The reason that potassium chloride does not cause embrittlement is thought to be because mixed potassium and silver complex ions of charge < 3- are formed in this case⁸⁰, see Table II.

(iii) Fractographic studies of both poly- and monocrystal specimens indicated that striae existed, Fig. 12⁷. These markings, which were perpendicular to the direction of crack propagation, were considered to result from a discontinuous fracture process, caused by the inability of the slowly diffusing complex ions to keep up with the advancing crack⁷.

While the preceding observations are consistent with an adsorption-dependent mechanism, they cannot be explained in terms of a dissolution-dependent model.

The observations on silver chloride would appear to support, by analogy, the view that an adsorption-dependent process is operative in stress-corrosion cracking of metals^{29,49,71}, and that the role of corrosion may be

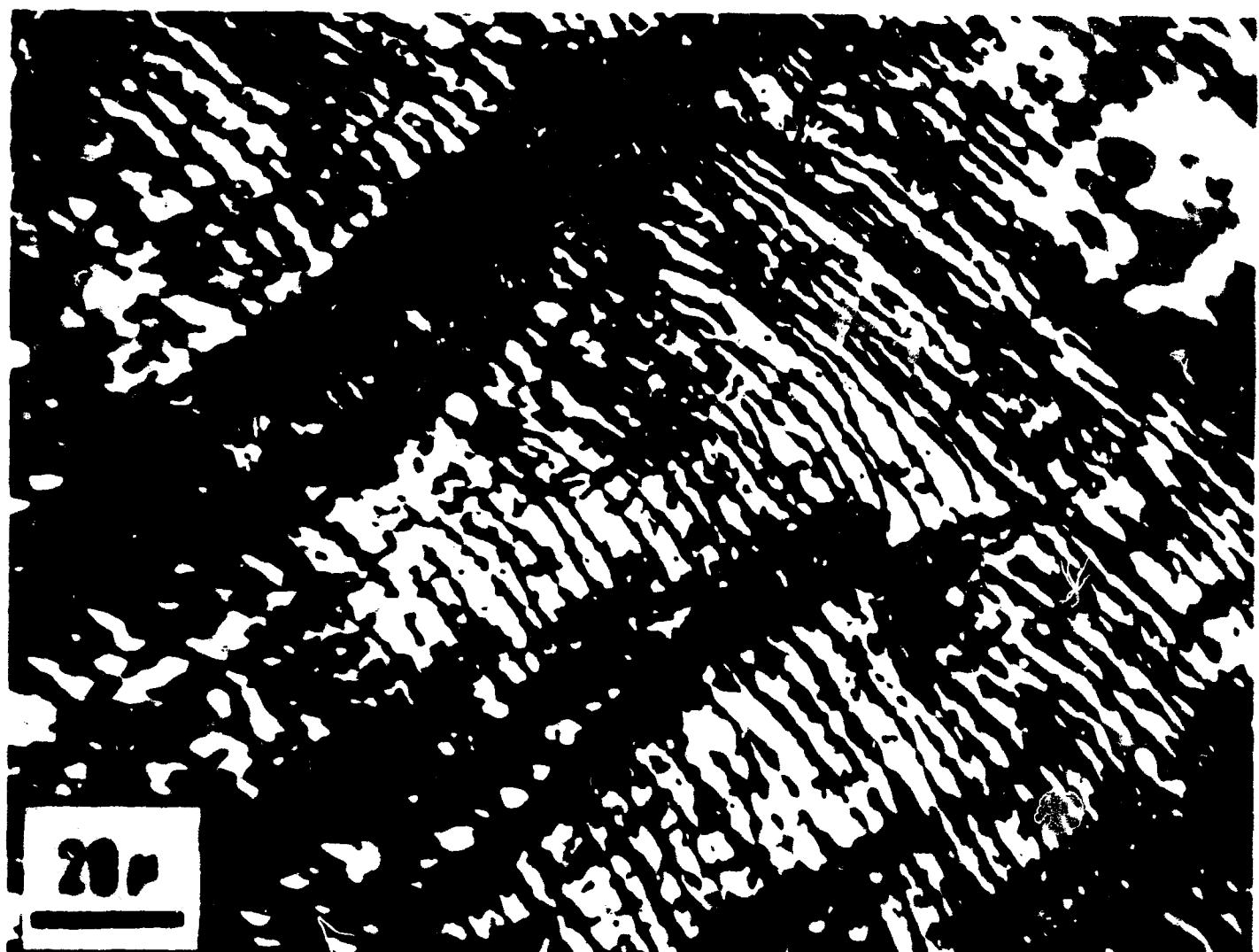


Fig. 1^c - Fracture surface of a single crystal of silver chloride stressed in 6N sodium chloride solution presaturated with AgCl_4^{3-} ions, illustrating striæ. The direction of crack propagation is indicated by the arrow. Bright field. (Westwood et al.⁷)

to produce (via dissolution) the specific ion species responsible for cracking²⁹. In this connection, the failure of α -brass in ammoniacal environments is of particular interest, because dissolution of copper in such environments leads to the formation of cupric complex ions of the general type $\text{Cu}(\text{NH}_3)_n^{2+}$ ³¹. Moreover, it has been demonstrated³²⁻³⁵ that the life of brass specimens in aqueous ammonia is markedly reduced when large concentrations of these ions are introduced into the solution before the test commences, e.g. Fig. 1³⁵. By analogy with the observations on the embrittlement of silver chloride, these results suggest that failure in brass may also result from adsorption of complex ions. However, it will be seen in the following section that this is not the case.

The possibility that the role of corrosion is simply to provide the embrittling ion species has been investigated²³ by comparing stress-corrosion life in "fresh" and "preconcentrated" solutions for (i) a magnesium-aluminum alloy in aqueous sodium chloride - sodium chromate solution, (ii) an age-hardened commercial aluminum alloy (2024) in aqueous sodium chloride, and (iii) a 304 austenitic stainless steel in boiling 40% magnesium chloride solution*. In each case, the testing solutions were presaturated by the addition of filings obtained from the material to be tested. No significant variation in times to failure at a given stress were noted for any of the systems, e.g. see Fig. 1.

* The experiments on the stainless steel were carried out by E. E. Denhard, Armco Steel Corporation, Baltimore.

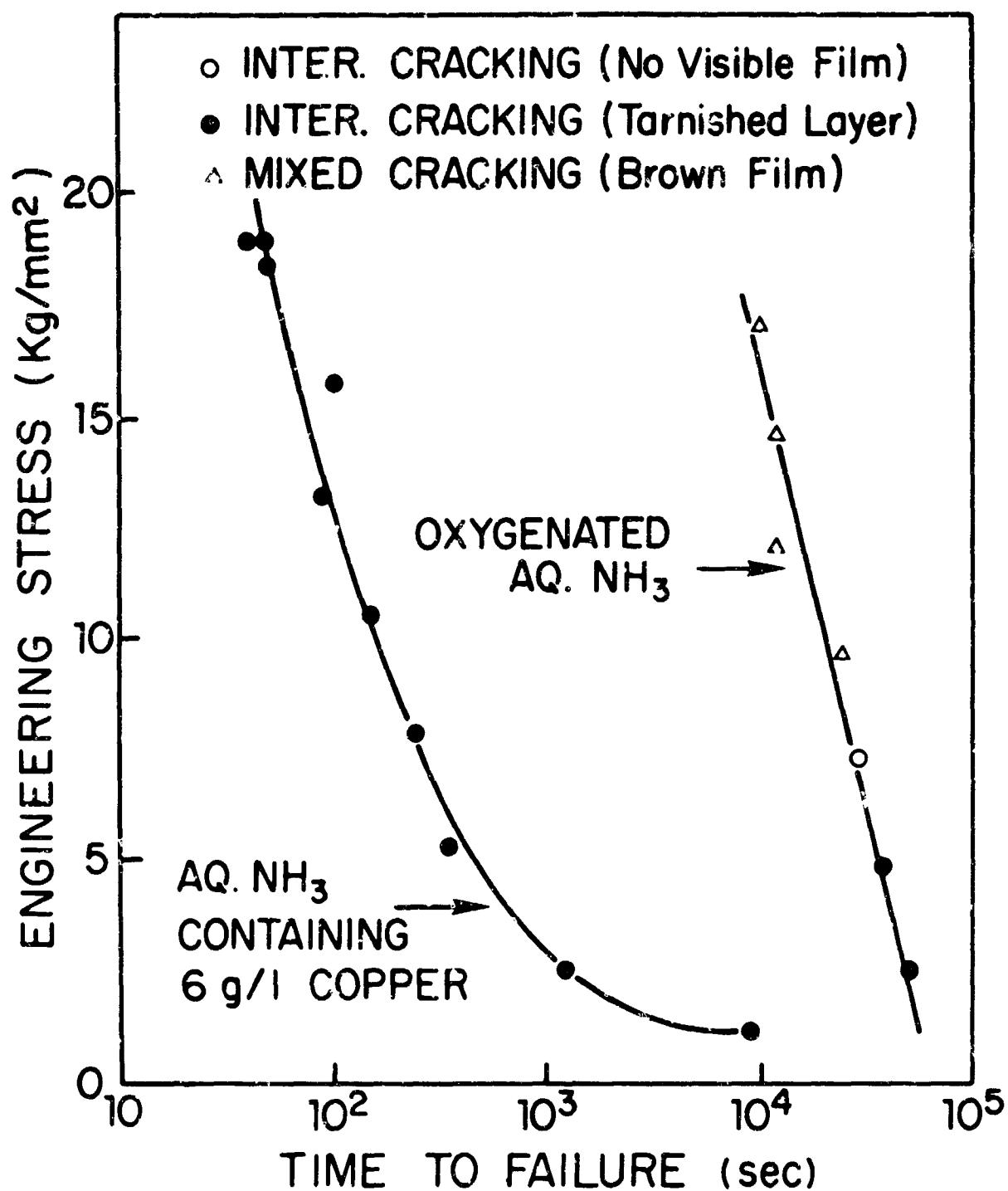


Fig. 1: Stress-corrosion data for α -brass stressed in oxygenated concentrated aqueous ammonia ($\sim 15\text{N}$), and in concentrated aqueous ammonia containing 6 g/l copper. The copper exists in solution as the complex ion $\text{Cu}(\text{NH}_3)_5^{2+}$. (Pugh et al.⁸⁵)

It is concluded, then, that while there is good evidence for an adsorption-dependent mechanism for the embrittlement of the non-metal silver chloride in aqueous environments, there is not, as yet, any unambiguous experimental support for such a process in metals.

A significant advance in our understanding of stress-corrosion cracking in α -brass has followed the recent proposal by Forty and Humble⁸⁶ that cracking in certain ammoniacal solutions proceeds by the repeated formation and rupture of a characteristic black oxide layer, commonly termed the tarnish. The process is illustrated schematically in Fig. 14. The first stage involves the formation and rupture of the tarnish, Fig. 14(a) and Fig. 14(b). An essential feature of the theory is that the crack does not propagate into the brass substrate, but becomes blunted by plastic deformation in the brass, Fig. 14(c)*. Fresh brass is then exposed to the tarnishing solution, allowing the process to be repeated, Fig. 14(d) - 14(f). Cracking thus proceeds in a discontinuous fashion, producing a fracture surface similar to that illustrated in Fig. 14(g).

Evidence for the tarnish-rupture model is convincing:

(i) Fractographic studies by McEvily and Bond²⁸ established that striae exist on stress-corrosion fracture surfaces, and that they were perpendicular to the direction of crack propagation, Fig. 15. This is strong evidence for discontinuous cracking, and is thus fully consistent with the tarnish-rupture model, cf. Fig. 15 and 14(g).

* This is in contrast to an earlier suggestion by Forty⁸⁷ that a crack initiated in brittle surface layers could propagate for a finite distance into the substrate.

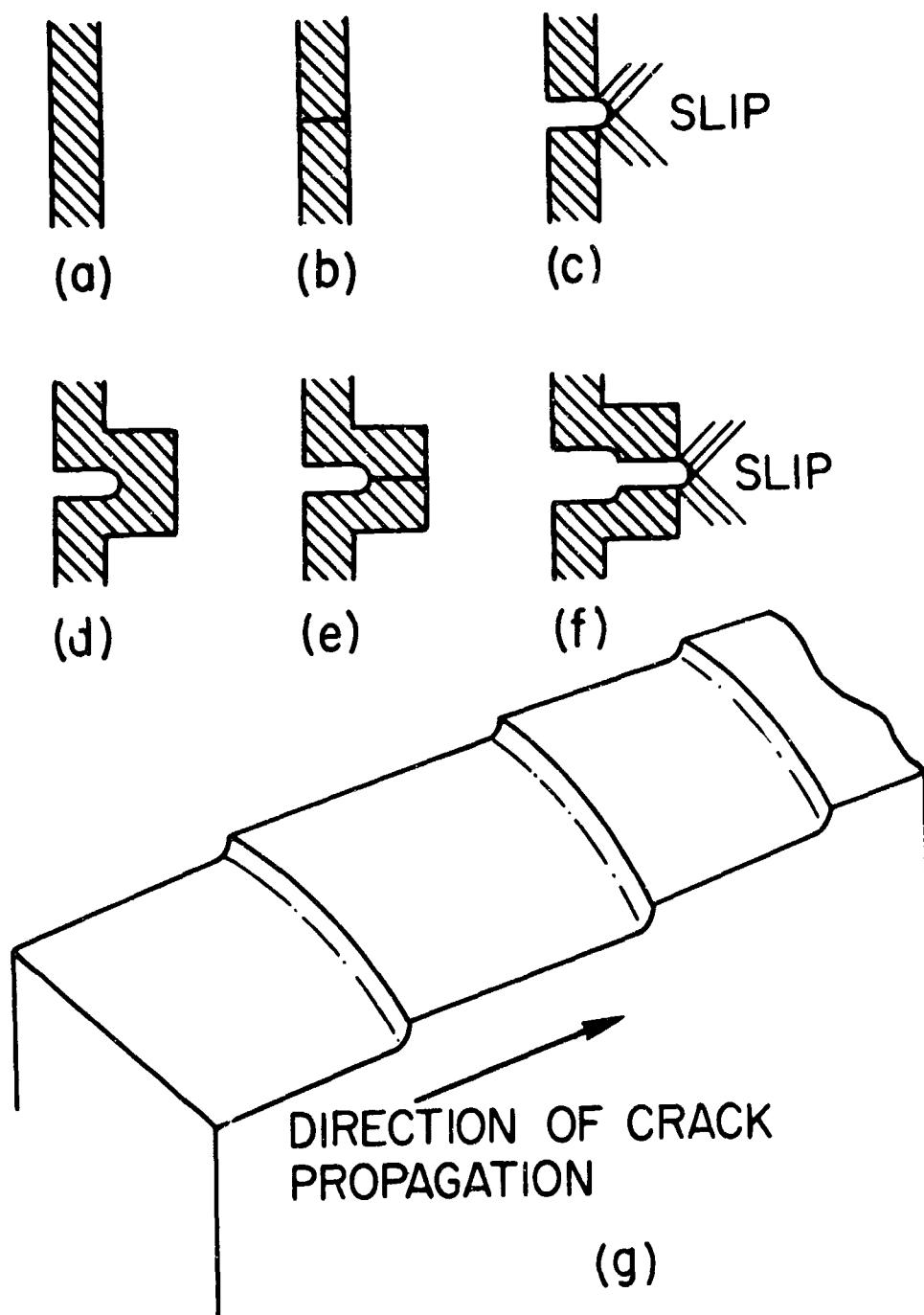


Fig. 14- (a) through (f). Schematic representation of tarnish-rupture mechanism for stress-corrosion cracking of brass. (g) Resulting fracture surface.



Fig. 15- Electron micrograph of replica of stress-corrosion fracture surface in α -brass. Note striae. (After McEvily and Bond²⁸.)

(ii) Forty and Humble⁸⁶ have shown that "crack-like penetrations" can be produced in α -brass single crystals by repeated immersion of unstressed specimens followed by stressing in the absence of the environment. Intercrystalline cracks also can be propagated in this fashion²³. For example, Fig. 16(a) illustrates part of an intercrystalline crack (the tip is marked by the arrow) in a specimen that was immersed unstressed in a tarnishing solution for 10 min, and then washed, dried, and plastically deformed in air by means of a manually operated jig. Note that the brass substrate is visible at the base of the crack, Fig. 16(a); cf. Fig. 14(c). When the specimen was re-immersed for a further 10 min, the base of the crack became tarnished, Fig. 16(b); cf. Fig. 14(d). The specimen was then stressed and the crack shown in Fig. 16 observed by means of an optical microscope. By "pulsing" the stress it was possible to propagate the crack discontinuously to the grain-boundary triple point A, where it joined a second crack which propagated from B. In addition, the crack became deeper, the brass substrate being barely discernible, Fig. 16(c); cf. Fig. 14(f). Repeated cycles led to complete intercrystalline failure.

The extent of crack propagation during each stressing operation is limited by the depth to which the tarnishing reaction has advanced beyond the crack tip. Thus continued stressing during an intermediate stage resulted in blunting of the cracks, and final fracture was ductile. The number of cycles necessary to cause failure could be controlled by varying the time of immersion. It was interesting to note that grain boundaries of specimens immersed for many hours became completely penetrated by the tarnish, and it was then possible to fracture the specimens into many small pieces manually. Fracture was completely intercrystalline in these cases.

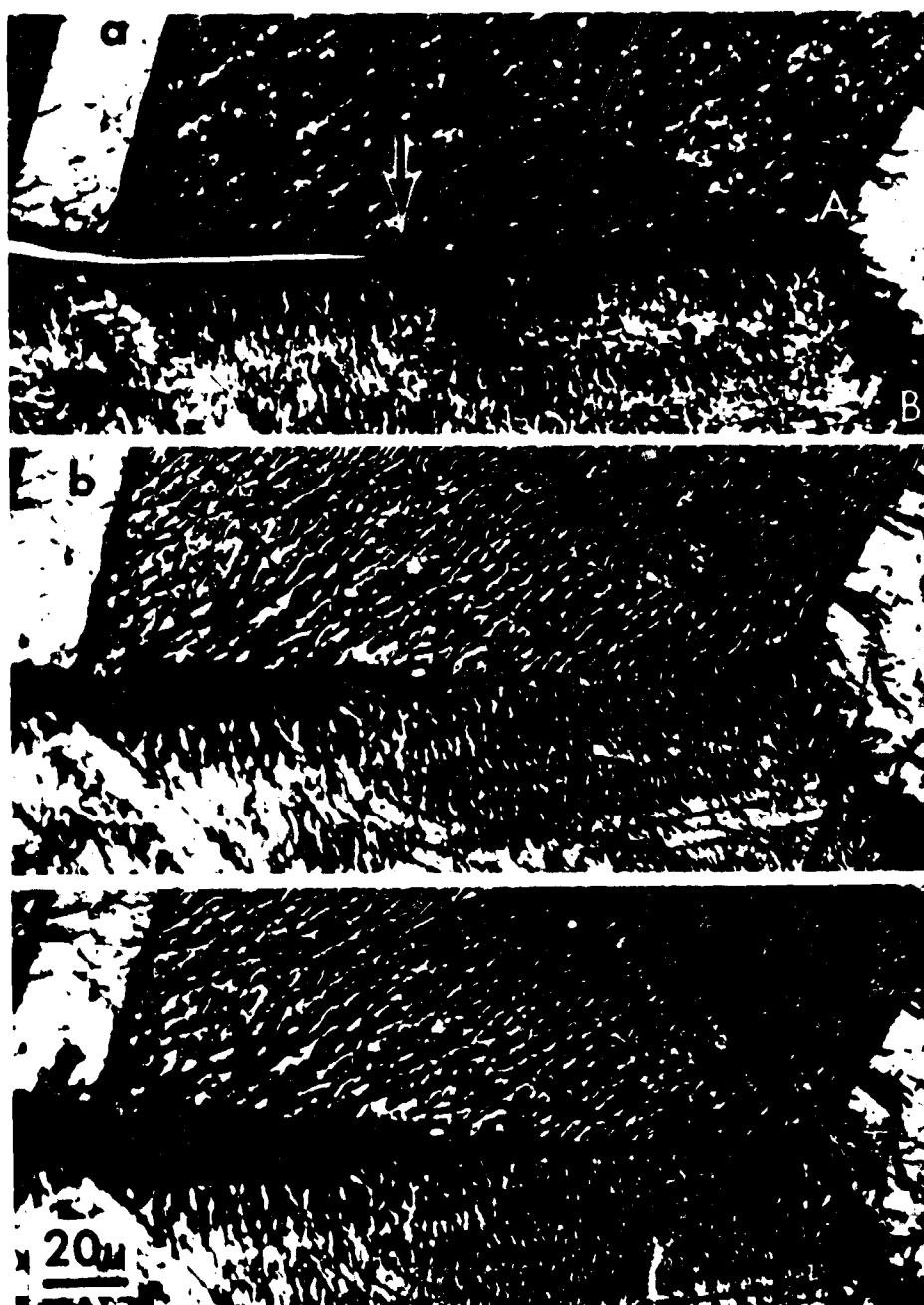


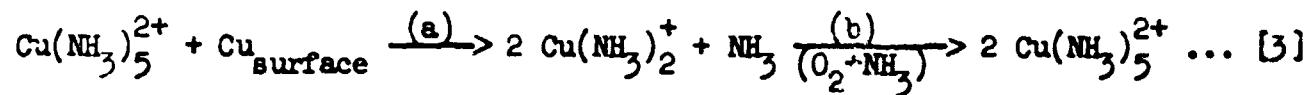
Fig. 16- Illustrating the propagation of an intercrystalline crack in α -brass by immersing an unstressed specimen in a tarnishing solution followed by stressing in air. See text for details. (Pugh and Westwood⁴⁶.)

Specimens ruptured in this fashion were closely similar in appearance to those tested in conventional tests where the stress was applied while the specimens were immersed in solution. Note that these observations would appear to invalidate the classical definition of Sutton et al.³ (see above), according to which stress-corrosion cracking requires the simultaneous action of stress and corrosive attack.

The preceding observations provide strong support for the tarnish-rupture theory. Moreover, they cannot be reconciled with dissolution models, such as that proposed by Graf and Richter⁸³. However, the mechanism of tarnish rupture is not fully understood. In single crystals, the morphology of cracks in the tarnish has been shown to be related to the slip vector in the underlying brass⁸⁶. However, cracking in polycrystalline specimens is predominantly intercrystalline, and McEvily and Bond²⁸ have presented evidence that massive deformation of the substrate is not necessary for tarnish rupture. These workers have suggested that cracking may involve both dislocation motion in the tarnish, and epitaxial stresses. Recent work²³ has indicated that the original grain boundaries of the brass are maintained in the oxide, and it is possible therefore that these act as barriers to dislocation motion (within the tarnish), resulting in the initiation of intercrystalline cracks. Further work is necessary to investigate the possibility of such a semi-brittle process.

While the tarnish-rupture model accounts for stress-corrosion cracking in tarnished brass, there is evidence that failure also can occur in ammoniacal solutions which do not cause tarnishing^{16,46,85}. For example,

it has been reported that both stress-corrosion life, t_p , and surface condition of brass specimens tested in concentrated ($\sim 15N$) aqueous ammonia depend on the concentration of the complex ion $Cu(NH_3)_5^{2+}$ present in the environment⁴⁶. Figure 17(a) illustrates the relationship between t_p for specimens tested under a constant load and the copper content of the solutions, which in these experiments was directly proportional to the complex-ion concentration. The concentration at which the well-defined inflection occurred (~ 2.7 g/l copper) was found to correspond to the onset of tarnishing -- that is, specimens tested in solutions of lower concentration were tarnish-free, while in solutions of higher concentration they were tarnished. The onset of tarnishing also was reflected by a maximum in the relationship between the rate of weight loss and the copper content of the solution, Fig. 17(b). The initial increasing rates of weight loss with increasing copper content has been shown⁸⁵ to result from the following auto-catalytic reaction between $Cu(NH_3)_5^{2+}$ ions and copper at the brass surface:



Stage (a) of this reaction was considered to occur only at tarnish-free brass surfaces, so that the appearance of the tarnish causes a decreasing rate of weight loss.

These and other observations indicated that two mechanisms of stress-corrosion cracking are operative in α -brass⁴⁶. The mechanism of failure in the absence of the tarnish was not fully explained. The fact that decreasing t_p with increasing copper content was accompanied with

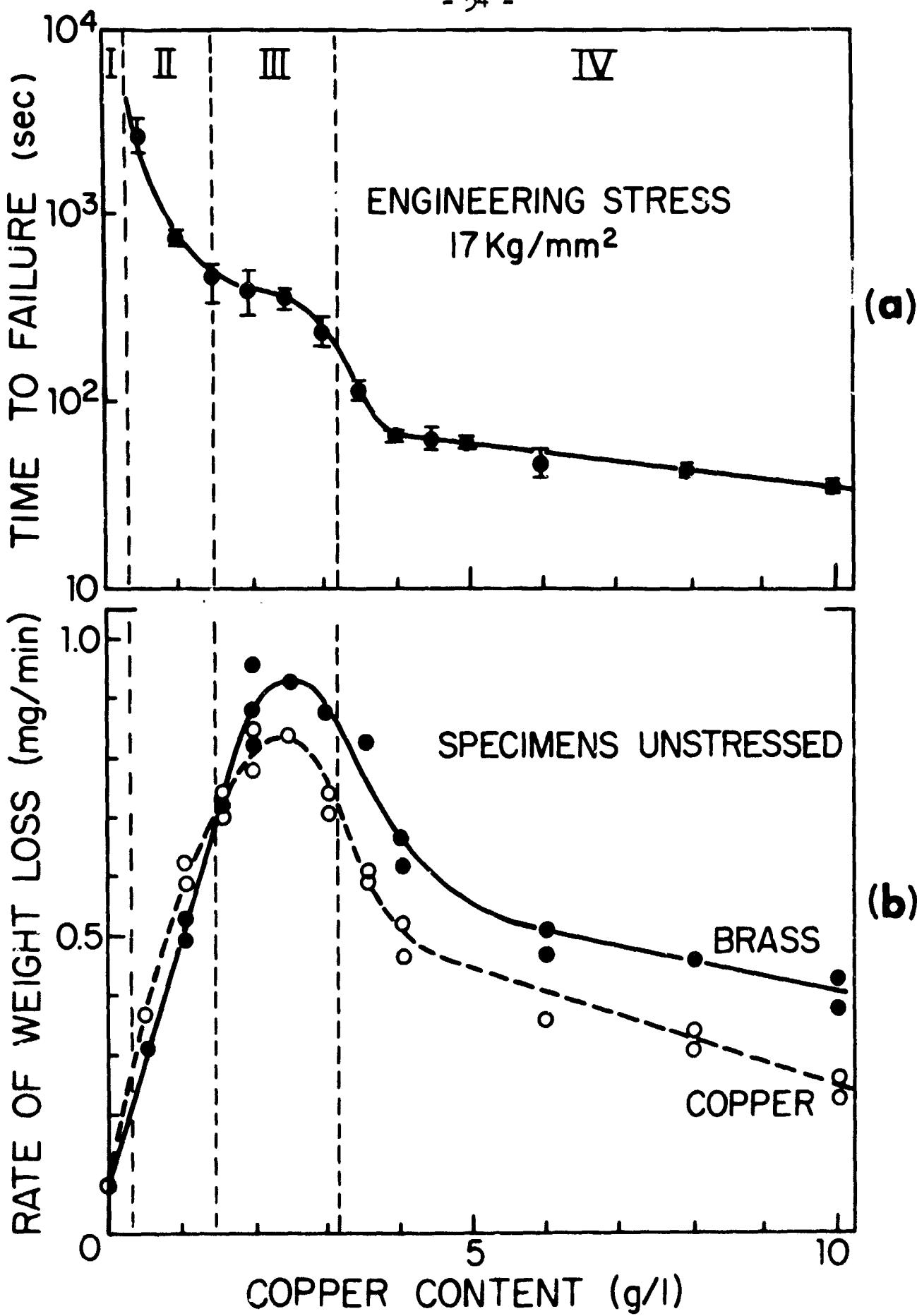
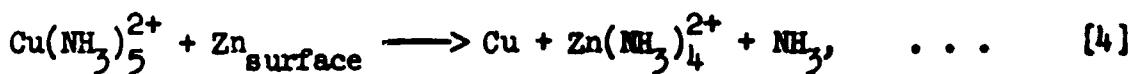


Fig. 17- Effect of copper content of ammonia environment on (a) time to failure of α -brass, and (b) rate of weight loss of unstressed brass and copper specimens. The copper exists in solution as the cupric complex ion $\text{Cu}(\text{NH}_3)_5^{2+}$; the concentration of the latter is directly proportional to the copper content of the solutions. (Pugh and Westwood⁴⁶.)

increased rates of weight loss, cf. Figs. 17(a) and 17(b), was considered to rule out the possibility of an adsorption-dependent mechanism similar to that thought to occur in silver chloride. Note that in the latter case, pre-saturated solutions caused no detectable weight loss⁶. On the other hand, the evidence was consistent with the dissolution model proposed by Tromans and Nutting³⁶. The preferential removal of zinc, which was seen (above) to be a prerequisite for this model, was thought to result from an exchange reaction between $\text{Cu}(\text{NH}_3)_5^{2+}$ ions and zinc,



occurring at the tarnish-free surface.

Consideration of the role of the complex ion $\text{Cu}(\text{NH}_3)_5^{2+}$ has led to the development of a model for tarnishing, according to which the formation of a detectable tarnish depends on two competing processes, namely (i) growth of tarnish and (ii) dissolution of tarnish⁴⁶. Tarnish growth was considered to depend on the rate of supply of oxygen to the tarnish surface, and also on the rates of diffusion of the anions and cations in the tarnish layer. It was proposed that the high rates of diffusion necessary for tarnish growth result from the preferential removal of zinc from the tarnish surface, which in effect injects vacancies into the layer*. Note that a detectable tarnish is not formed on copper surfaces. The preferential removal of zinc was thought to occur by reaction with $\text{Cu}(\text{NH}_3)_5^{2+}$ ions, by reaction [4]. The rate of dissolution of the tarnish was found to depend strongly on NH_4^+ concentration. Thus by controlling the concentration of these ions it was shown

* This approach is based on an earlier suggestion by Forty⁸⁷ which involved de-zincification at essentially film-free brass surfaces.

that the copper content of the solution at which tarnishing occurred could be varied significantly.

According to the preceding discussion, the specific action of oxygenated aqueous ammonia in causing stress-corrosion cracking in α -brass stems from the presence of cupric complex ions such as $\text{Cu}(\text{NH}_3)_5^{2+}$ ($\text{Cu}(\text{NH}_3)_4^{2+}$ ions have been found to behave similarly⁸⁵). The role of these ions appears to be to preferentially remove zinc, via reaction [4], from both tarnished and tarnish-free brass surfaces.

These considerations also are relevant to practical aspects of stress-corrosion cracking in brass. For example, season cracking is commonly observed in moist industrial atmospheres. Under these conditions, it has been suggested that shallow layers of adsorbed water can pick up oxygen and ammonia, thus setting up conditions favoring the formation of large concentrations of cupric complex ions and hence causing cracking⁸⁵. Similarly, it is well known that failure in stressed specimens partially immersed in aqueous ammonia generally occurs at, or just above, the level of the solution. This effect can be attributed to conditions within the meniscus i.e. small volume and ready access of oxygen, which again leads to the formation of large complex-ion concentrations^{83,85}.

The success of the tarnish-rupture theory in accounting for stress-corrosion cracking in tarnished brass necessitates a re-examination of failures in other systems to determine whether a similar mechanism may be operative. There already is evidence that oxide rupture plays an important role in the cracking of gamma uranium alloys in certain aqueous environments⁹⁸.

Moreover, the observations of Nielsen⁵¹ on the failure of austenitic stainless steel in boiling magnesium chloride solutions are of particular interest in this connection. Electron-microscope studies of corrosion products removed from within stress-corrosion cracks revealed that a "terraced" or "laminated" topography existed, Fig. 18. The occurrence of the surface markings was not explained at that time, but it is now attractive to speculate that they correspond to the striae observed in the case of brass, Fig. 15. It must be emphasized, however, that the existence of striae on fracture surfaces does not necessarily indicate that fracture involves the rupture of a brittle film. For example, such markings were observed in the case of embrittled silver chloride, Fig. 12, but there is little possibility of the formation of brittle surface films in that material. Further study, e.g. experiments similar to those carried out in α -brass, in which unstressed specimens are immersed in the environment and then stressed in the absence of the environment (see Fig. 16), is necessary to determine whether a (brittle) film-rupture mechanism is operative in austenitic stainless steel.

CONCLUSIONS

While many aspects of stress-corrosion cracking remain obscure, it is concluded that sufficient evidence now exists to rule out the existence of a generalized theory. In aged aluminum alloys, failure is considered to be mechanical, resulting from corrosion-induced creep in the



Fig. 18- Transmission electron micrograph of corrosion product taken from within a stress-corrosion crack in austenitic stainless steel. Note "striæ". (After Nielsen⁵¹.)

precipitate-free zones at grain boundaries. There is strong evidence that the failure of α -brass in certain ammoniacal environments occurs by the repeated formation and rupture of the brittle tarnish layer. However, failure also occurs in this system under conditions when no tarnish is formed, indicating that a second mechanism is operative. The latter is not fully understood, but it is suggested that it may involve a dissolution-dependent mechanism of the type proposed by Trowans and Nutting³⁶, that is, by the preferential dissolution at dislocations, generated during the stress-corrosion process, which are made chemically reactive by segregation of zinc atoms to these sites. Embrittlement of the non-metal silver chloride in certain complex-forming environments is thought to occur by an adsorption-dependent mechanism. However, there is no unambiguous evidence, as yet, for such a mechanism in metals.

Stress-corrosion cracking in many other commercially important systems remains to be explained. The success of the tarnish-rupture mechanism in the case of brass clearly necessitates a re-examination of these failures to determine whether a similar mechanism is operative. In the longer term, it is evident that any real understanding of the problem in any particular system requires a knowledge of the specific action of the environment. The role of chloride ions in the stress-corrosion cracking of austenitic stainless steels is a case which warrants immediate attention.

ACKNOWLEDGEMENTS

The author is indebted to A. R. C. Westwood for many helpful and stimulating discussions, and to the U. S. Army Research Office (Durham) for financial support.

REFERENCES

1. H. R. Copson: Stress Corrosion Cracking and Embrittlement, p. 187, John Wiley, New York, 1956.
2. W. L. Williams: Corrosion, 1961, vol. 17, p. 340t.
3. H. Sutton, E.A.G. Liddiard, B. Chalmers, and F. A. Champion: J. Inst. Metals, 1945, vol. 71, p. xvii.
4. R. B. Mears, R. H. Brown, and E. H. Dix, Jr.,: Symposium on Stress-Corrosion Cracking of Metals, p. 323, ASTM-AIME, Philadelphia, 1944.
5. A.R.C. Westwood, E. N. Pugh, and D. L. Goldheim: Phil. Mag., 1964, vol. 10, p. 345.
6. A.R.C. Westwood, D. L. Goldheim, and E. N. Pugh: Disc. Faraday Soc., 1964, No. 38, p. 147.
7. A.R.C. Westwood, D. L. Goldheim, and E. N. Pugh: Grain Boundaries and Surfaces in Ceramics, Plenum Press, New York, 1965, in press.
8. A.R.C. Westwood, D. L. Goldheim, and E. N. Pugh: Acta Met., 1965, vol. 13, p. 695.
9. Symposium on Stress-Corrosion Cracking of Metals, ASTM-AIME, Philadelphia, 1944.
10. Stress-Corrosion Cracking and Embrittlement, John Wiley, New York, 1956.
11. Physical Metallurgy of Stress-Corrosion Fracture, Interscience, New York, 1959.
12. S. Barnartt: Corrosion, 1962, vol. 18, p. 322t.
13. A.R.C. Westwood: Fracture of Solids, p. 553, Interscience, New York, 1963.

14. R. N. Parkins: Met. Rev., 1964, vol. 9, p. 201.
15. D. K. Priest: Ref. 10, p. 81.
16. E. Mattsson: Electrochimica Acta, 1961, vol. 3, p. 279.
17. H. J. Engell and A. Baumel: Ref. 11, p. 341.
18. J. N. Wanklyn and P. J. Jones: J. Nuclear Mat., 1962, vol. 6, p. 291.
19. R. Franks, W. O. Binder, and C. M. Brown: Ref. 9, p. 411.
20. A. R. Bailey: Met. Rev., 1961, vol. 6, p. 101.
21. L. Graf: Metall, 1964, vol. 18, p. 1163.
22. D. H. Thompson: Anaconda American Brass Co., Private Communication.
23. E. N. Pugh, W. G. Montague, and A.R.C. Westwood: 1965, unpublished work.
24. J. J. Harwood: Ref. 10, p. 1.
25. W. D. Robertson and A. S. Tetelman: Strengthening Mechanisms in Solids, p. 217, ASM, Cleveland, 1962.
26. C. W. George and B. Chalmers: Ref. 9, p. 345.
27. G. Edmunds: ibid., p. 67.
28. A. J. McEvily, Jr., and A. P. Bond: J. Electrochem. Soc., 1965, vol. 112, p. 131.
29. E. G. Coleman, D. Weinstein, and W. Rostoker: Acta Met., 1961, vol. 9, p. 491.
30. T. P. Hoar and J. M. West: Proc. Roy. Soc., 1962, vol. A268, p. 304.
31. T. P. Hoar and J. C. Scully: J. Electrochem. Soc., 1964, vol. 111, p. 348.
32. L. J. Petch: J. Iron Steel Inst., 1953, vol. 174, p. 25.
33. A. N. Stroh: Proc. Roy. Soc., 1955, vol. A232, p. 548.

34. G. Thomas: Proc. Sec. Int. Mat. Conf., Berkeley, 1964, in press.
35. J. Flis: Bull. Acad. Polon. Sci., Ser. Sci. Chim., 1963, vol. 11, p. 23.
36. D. Tromans and J. Nutting: Fracture of Solids, p. 637, Interscience, New York, 1963.
37. S. Barnartt, R. Stickler, and D. van Rooyen: Corrosion Science, 1963, vol. 3, p. 9.
38. P. R. Swann: Corrosion, 1963, vol. 19, p. 102t.
39. M. J. Whelan: Proc. Roy. Soc., 1958, vol. A249, p. 114.
40. C. Edeleanu: J. Iron Steel Inst., 1953, vol. 175, p. 390.
41. H. R. Copson: Ref. 11, p. 247.
42. K. C. Thomas, R. Stickler, and R. J. Allio: Corrosion Science, 1965, vol. 5, p. 71.
43. M. N. Saxena and R. A. Dodd: Environment-Sensitive Mechanical Behavior, p. , Gordon and Breach, New York, 1965.
44. D. H. Thompson and A. W. Tracy: AIME Trans., 1949, vol. 185, p. 100.
45. P. R. Swann and J. Nutting: J. Inst. Metals, 1961-62, vol. 90, p. 133.
46. E. N. Pugh and A.R.C. Westwood: to be published.
47. A. Howie and P. R. Swann: Phil. Mag., 1961, vol. 6, p. 1215.
48. E. H. Dix: AIME Trans., 1940, vol. 137, p. 11.
49. H. H. Uhlig: Ref. 11, p. 1.
50. J. G. Hines: Corrosion Science, 1961, vol. 1, p. 121.
51. N. A. Nielsen: Ref. 11, p. 121.
52. F. A. Champion: Symposium of Internal Stresses in Metals and Alloys, p. 468, Inst. of Metals, London, 1948.

53. H. L. Logan: J. Res. Nat. Bur. Stds., 1952, vol. 48, p. 99.
54. H. L. Logan: J. Res. Nat. Bur. Stds., 1958, vol. 61, p. 503.
55. P. R. Swann and J. D. Embury: Proc. Sec. Int. Mat. Conf., Berkeley, 1964, in press.
56. H. W. Pickering and P. R. Swann: Corrosion, 1963, vol. 19, p. 373t.
57. N. A. Nielsen: Corrosion: 1964, vol. 20, p. 104t.
58. A.R.C. Westwood: Environment-Sensitive Mechanical Behavior, p. , Gordon and Breach, New York, 1965.
59. A.R.C. Westwood and H. Rubin: J. Appl. Phys., 1962, vol. 33, p. 2001.
60. G. W. Sears: J. Chem. Phys., 1960, vol. 32, p. 1317.
61. D. N. Staicopolus: J. Electrochem. Soc., 1961, vol. 108, p. 900.
62. T. P. Hoar and J. G. Hines: Ref. 10, p. 107.
63. S. Barnartt and D. van Rooyen: J. Electrochem. Soc., 1961, vol. 108, p. 222.
64. G. Thomas and J. Nutting: J. Inst. Metals, 1959-60, vol. 88, p. 81.
65. E. N. Pugh and W.R.D. Jones: Metallurgia, 1961, vol. 63, p. 3.
66. P. T. Gilbert and S. E. Hadden: J. Inst. Metals, 1950, vol. 77, p. 237.
67. D. van Rooyen: Corrosion, 1960, vol. 16, p. 421t.
68. G. Meikle: J. Inst. Metals, 1956-57, vol. 85, p. 540.
69. E. N. Pugh: Ph.D. Thesis, University of Wales, 1959.
70. P.J.E. Forsyth and D. A. Ryder: Metallurgia, 1961, vol. 63, p. 117.
71. H. Nichols and W. Rostoker: Trans. Am. Soc. Metals, 1963, vol. 56, p. 494.
72. N. J. Petch and P. Stables: Nature, 1953, vol. 169, p. 842.

73. N. J. Petch: Phil. Mag., 1956, vol. 1, p. 331.
74. C. Edeleanu: Ref. 11, p. 97.
75. H. Nichols and W. Rostoker: Acta Met., 1961, vol. 9, p. 504.
76. A.R.C. Westwood and M. H. Kamdar: Phil. Mag., 1963, vol. 8, p. 787.
77. N. S. Stoloff and T. L. Johnston: Acta Met., 1963, vol. 11, p. 251.
78. L. Pauling: The Nature of the Chemical Bond, p. 73, Cornell Press, Ithaca, 1940.
79. J. Kratochvil, B. Tezak, and V. B. Vouk: Arhiv Za Kemiju (in English), 1954, vol. 26, p. 191.
80. C. Brink and C. H. McGillivry: Acta Cryst., 1949, vol. 2, p. 458.
81. F. A. Cotton and G. Wilkinson: Advanced Inorganic Chemistry, Interscience, New York, 1963.
82. F. C. Althof: Z. Metall., 1944, vol. 36, p. 177.
83. L. Graf and W. Richter: Z. Metall., 1961, vol. 52, p. 833.
84. E. N. Pugh and A.R.C. Westwood: Proc. Sec. Int. Mat. Conf., Berkeley, 1964, in press.
85. E. N. Pugh, W. G. Montague, and A.R.C. Westwood: 1965, to be published.
86. A. J. Forty and P. Humble: Phil. Mag., 1963, vol. 8, p. 247.
87. A. J. Forty: Ref. 11, p. 99.
88. J. N. Chirigos: Ref. 11, p. 70.